

PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

PCT

NOTIFICATION OF TRANSMITTAL OF
THE INTERNATIONAL SEARCH REPORT
OR THE DECLARATION

(PCT Rule 44.1)

To:
SUZUKI & ASSOCIATES
Attn. Suzuki, Shunichiro
Gotanda Yamazaki Bldg. 6F,
13-6, Nishigotanda 7-chome
Shinagawa-ku, Tokyo 141-0031
JAPAN

Date of mailing
(day/month/year) 01/03/2002

Applicant's or agent's file reference
SF-762

FOR FURTHER ACTION See paragraphs 1 and 4 below

International application No.
PCT/JP 01/06003

International filing date
(day/month/year) 11/07/2001

Applicant

SHOWA DENKO K.K. et al.

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

Filing of amendments and statement under Article 19:

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

When? The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

Where? Directly to the International Bureau of WIPO
34, chemin des Colombettes
1211 Geneva 20, Switzerland
Facsimile No.: (41-22) 740.14.35

For more detailed instructions, see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.


4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis.1 and 90bis.3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority

 European Patent Office, P.B. 5818 Patentlaan 2
NL-2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Eva Bleijs

TENT COOPERATION TREATY

PCT

INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference SF-762	FOR FURTHER ACTION <small>see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.</small>	
International application No. PCT/JP 01/06003	International filing date (day/month/year) 11/07/2001	(Earliest) Priority Date (day/month/year) 19/07/2000
Applicant SHOWA DENKO K.K. et al.		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.
☒ It is also accompanied by a copy of each prior art document cited in this report.

1. Basis of the report

- a. With regard to the **language**, the international search was carried out on the basis of the international application in the language in which it was filed, unless otherwise indicated under this item.
- ☐ the international search was carried out on the basis of a translation of the international application furnished to this Authority (Rule 23.1(b)).
- b. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international search was carried out on the basis of the sequence listing :
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ the statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ the statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished

2. ☐ **Certain claims were found unsearchable** (See Box I).

3. ☐ **Unity of invention is lacking** (see Box II).

4. With regard to the title,

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established by this Authority to read as follows:

5. With regard to the abstract,

- ☒ the text is approved as submitted by the applicant.
- ☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international search report, submit comments to this Authority.

6. The figure of the **drawings** to be published with the abstract is Figure No.

- ☐ as suggested by the applicant.
- ☐ because the applicant failed to suggest a figure.
- ☐ because this figure better characterizes the invention.

☒ **None of the figures.**

INTERNATIONAL SEARCH REPORT

National Application No

PCT/JP 01/06003

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C69/60 C07C67/333 C08F22/26 C08L67/06 C08G63/21

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07C C08F C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

CHEM ABS Data, EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JOHANSSON, MATS ET AL: "Influence of allyl ethers in coating resins" J. POLYM. SCI., PART A: POLYM. CHEM. (1991), 29(11), 1639-44 , XP002188713 page 1641 page 1643	2,6,26, 29
A	the whole document	1,10,13, 15,30
X	KLABAN, JIRI ET AL: "Infrared spectroscopic study of polymerization of bis(glycerol monoallyl ether)fumarate" J. POLYM. SCI., POLYM. SYMP. (1967), 16 247-56 , XP002188714 page 247 page 252 -page 256	2,6,26, 29

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

13 February 2002

Date of mailing of the international search report

01/03/2002

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
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Fax: (+31-70) 340-3016

Authorized officer

Kardinal, S

INTERNATIONAL SEARCH REPORT

International Application No
PCT/JP 01/06003

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 278 559 A (REINHARDT HEINZ F) 11 October 1966 (1966-10-11) example 1 ---	2,6
X	GB 1 188 112 A (L. A. BASHFORD) 15 April 1970 (1970-04-15) cited in the application example 1	2,6,26, 29
A	the whole document	1,10,13, 15-19,30
X	US 2 514 786 A (CROXALL WILLARD J ET AL) 11 July 1950 (1950-07-11) example 1 ---	2,6
X	EP 0 957 079 A (SHOWA DENKO KK) 17 November 1999 (1999-11-17) claims 7-9; examples 1,2,6,8 the whole document	2,6, 22-26,29
A	----- the whole document	1,10,13, 15-19,30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 01/06003

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3278559	A	11-10-1966	NONE	
GB 1188112	A	15-04-1970	NONE	
US 2514786	A	11-07-1950	NONE	
EP 0957079	A	17-11-1999	AU 8128598 A EP 0957079 A1 US 6204410 B1 WO 9902482 A1	08-02-1999 17-11-1999 20-03-2001 21-01-1999

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 January 2002 (24.01.2002)

PCT

10/088229
(10) International Publication Number
WO 02/06206 A3

- (51) International Patent Classification⁷: C07C 69/60, 67/333, C08F 22/26, C08L 67/06, C08G 63/21
- (74) Agent: SUZUKI, Shunichiro; SUZUKI & ASSOCIATES, Gotanda Yamazaki Bldg. 6F, 13-6, Nishigotanda 7-chome, Shinagawa-ku, Tokyo 141-0031 (JP).
- (21) International Application Number: PCT/JP01/06003
- (22) International Filing Date: 11 July 2001 (11.07.2001)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:
2000-218179 19 July 2000 (19.07.2000) JP
60/246,587 8 November 2000 (08.11.2000) US
2000-394580 26 December 2000 (26.12.2000) JP
- (71) Applicant (for all designated States except US): SHOWA DENKO K.K. [JP/JP]; 13-9, Shibadaimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): KAI, Kazufumi [JP/JP]; c/o OITA PLANT, PETROCHEMICALS SECTOR, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). OHTA, Keisuke [JP/JP]; c/o OITA PLANT, PETROCHEMICALS SECTOR, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). KADOWAKI, Yasushi [JP/JP]; c/o OITA PLANT, PETROCHEMICALS SECTOR, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). UCHIDA, Hiroshi [JP/JP]; c/o OITA PLANT, PETROCHEMICALS SECTOR, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
- Published:
— with international search report
— before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments
- (88) Date of publication of the international search report:
25 April 2002
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: FUMARATE DERIVATIVE, METHOD FOR PRODUCING THE SAME

(57) Abstract: This invention is to provide a polymerizable composition having excellent curability and surface hardness, and a cured product thereof. A novel fumarate derivative having two or more fumarate groups within one molecule and ensuring high copolymerizability with the terminal alkenyloxy group, a method for producing the derivative, a polymerizable composition containing the derivative, and a cured product thereof are provided.

WO 02/06206 A3

INTERNATIONAL SEARCH REPORT

International Application No

PCT/JP 01/06003

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C07C69/60 C07C67/333 C08F22/26 C08L67/06 C08G63/21

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B. FIELDS SEARCHED

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IPC 7 C07C C08F C08G C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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INTERNATIONAL SEARCH REPORT

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X	EP 0 957 079 A (SHOWA DENKO KK) 17 November 1999 (1999-11-17) claims 7-9; examples 1,2,6,8 A the whole document -----	2,6, 22-26,29
		1,10,13, 15-19,30

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/JP 01/06003

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GB 1188112	A	15-04-1970	NONE	
US 2514786	A	11-07-1950	NONE	
EP 0957079	A	17-11-1999	AU 8128598 A	08-02-1999
			EP 0957079 A1	17-11-1999
			US 6204410 B1	20-03-2001
			WO 9902482 A1	21-01-1999

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(43) International Publication Date
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WO 02/06206 A2

(51) International Patent Classification⁷: **C07C 69/60**,
67/333, C08F 22/26

(21) International Application Number: **PCT/JP01/06003**

(22) International Filing Date: **11 July 2001 (11.07.2001)**

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
2000-218179 19 July 2000 (19.07.2000) JP
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(71) Applicant (*for all designated States except US*): **SHOWA DENKO K.K.** [JP/JP]; 13-9, Shibadaimon 1-chome, Minato-ku, Tokyo 105-8518 (JP).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **KAI, Kazufumi** [JP/JP]; c/o OITA PLANT, PETROCHEMICALS SECTOR, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **OHTA, Keisuke** [JP/JP]; c/o OITA PLANT, PETROCHEMICALS SECTOR, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP). **KADOWAKI, Yasushi** [JP/JP]; c/o OITA PLANT, PETROCHEMICALS SECTOR, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189

(JP). **UCHIDA, Hiroshi** [JP/JP]; c/o OITA PLANT, PETROCHEMICALS SECTOR, SHOWA DENKO K.K., 2, Oaza Nakanosu, Oita-shi, Oita 870-0189 (JP).

(74) Agent: **SUZUKI, Shunichiro**; SUZUKI & ASSOCIATES, Gotanda Yamazaki Bldg. 6F, 13-6, Nishigotanda 7-chome, Shinagawa-ku, Tokyo 141-0031 (JP).

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

Published:

— without international search report and to be republished upon receipt of that report

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(54) Title: **FUMARATE DERIVATIVE, METHOD FOR PRODUCING THE SAME**

(57) Abstract: This invention is to provide a polymerizable composition having excellent curability and surface hardness, and a cured product thereof. A novel fumarate derivative having two or more fumarate groups within one molecule and ensuring high copolymerizability with the terminal alkenyloxy group, a method for producing the derivative, a polymerizable composition containing the derivative, and a cured product thereof are provided.

WO 02/06206 A2

DESCRIPTION**Fumarate Derivative, Method for Producing the Same****5 Cross-Reference to Related Application**

This application is an application filed under 35 U.S.C. §111(a) claiming benefit pursuant to 35 U.S.C. §119(e)(1) of the filing date of Provisional Application 60/246,587 filed November 8, 2000 pursuant to 35 U.S.C. §111(b).

10

Field of the Invention

The present invention relates to a novel fumarate derivative having excellent radical polymerizability, capable of giving a polymer by light or heat, and usable as a crosslinking agent for various polymers, particularly usable in the field where curing in the air is required, such as coating material, coating, adhesive and sealing material, and also relates to a method for producing the derivative, a polymerizable composition containing the derivative, and a cured product thereof.

15

20

Background of the Invention

Heretofore, polyfunctional compounds having a double bond have been used for many uses, for example, as a starting material or the like of polymerizable compositions.

These polymerizable compositions are cured
5 predominantly by radical polymerization under light or heat. In particular, a high-speed photopolymerization by an ultraviolet ray (UV) is recently employed from the standpoint of profitability. The polymerizable composition used for the high-speed photopolymerization is generally an
10 acrylic compound or an unsaturated carboxylic acid ester-type compound. However, these compounds have the following problems.

The acrylic compound as a crosslinked monomer can be cured within a relatively short time in UV curing and
15 therefore, is applied to various UV curing materials such as coating material and coating, however, this monomer has a problem in that the skin irritation is relatively high and since the compound is prone to curing inhibition by oxygen, stickiness is readily generated at the formation of
20 a thin film.

With respect to the unsaturated carboxylic acid ester-type compound, dialkyl esters of fumaric acid or maleic acid are known, however, these compounds are individually poor in the radical polymerization property and even when
25 copolymerized with another resin, the degree of

crosslinking is not sufficiently high and the cured product obtained may suffer from insufficient strength in some cases. Furthermore, the unsaturated polyester by itself has a large molecular weight and is poor in the

5 homopolymerizability, therefore, a styrene monomer is generally used as a reactive diluent. However, in view of workability such as odor, an alternative of the styrene monomer is demanded.

In order to overcome these problems, vinyl ethers as

10 one of alkenyl ethers are recently taken notice of as a non-acrylic compound.

The vinyl ethers are generally used as a curable material for cationic polymerization system. It is said that radical polymerization of the vinyl ether itself

15 scarcely proceeds when used alone, however, a report in Rad. Tech. North America, 167 (1992) states that copolymerization proceeds between maleate and vinyl ether.

Other than this, some examples of copolymerization systems are also known. U.S. Patents 5,334,455 and

20 5,334,456 describe a system where a polyfunctional vinyl ether is polymerized with a reactant between epoxy and maleic anhydride and a system where a polyfunctional vinyl ether is polymerized with a maleate, and Japanese Patent 2,705,916 describes a composition of an unsaturated

25 polyester and a vinyl ether.

In addition, the vinyl ether is known to copolymerize with an acrylate despite its low copolymerizability.

The vinyl ether is characterized by low viscosity, excellent diluting ability and high adhesion to a substrate at the curing but, as described above, exhibits poor radical polymerizability when used alone. Therefore, in the system where an unsaturated polyester or the like is blended, the vinyl ether group is incompletely polymerized to fail in bringing out the physical properties of the cured product and furthermore, the ratio of the other polymerizable group to the vinyl ether group in the polymerization must be adjusted, giving rise to a problem that the amount of vinyl ether used is limited.

In order to overcome these problems, JP-B-55-395533 (the term "JP-B" as used herein means an "examined Japanese patent publication") describes a method for producing a compound having a vinyl ether group at the terminal and having a maleate structure in the inside, and British Patent 1,188,112 describes a compound having an allyl ether group at the terminal and having a maleate or fumarate structure in the inside.

These polymerizable compounds have, however, only two polymerizable groups at the terminal and one polymerizable group in the inside and still cannot have a sufficiently large number of crosslinking points.

The object of the present invention is to provide a novel fumarate derivative which can overcome the problems in conventional radical polymerizable compounds, such as curing inhibition by oxygen at curing or low surface hardness of the cured product, and which has a sufficiently large number of crosslinking points. The object of the present invention includes providing a method for producing the derivative, a polymerizable composition containing the derivative, and a cured product thereof.

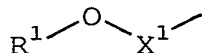
10

Disclosure of the Invention

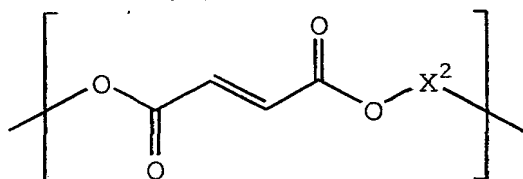
As a result of extensive investigations to solve the above-described problems, the present inventors have found a novel fumarate derivative polyfunctionalized to have an alkenyloxy group such as vinyl ether group, propenyl ether group or allyl ether group, and a fumarate group within the same molecule and further having many double bonds. The above-described objects can be attained by using this fumarate derivative as a radical polymerizable resin or a crosslinking agent for resin. The present invention has been accomplished based on this finding.

More specifically, the present invention (I) is a fumarate derivative having at least one group represented by formula (1) as the terminal groups and having two or more groups represented by formula (2) as a repeating unit:

Formula (1)

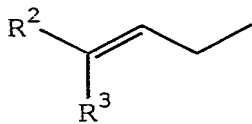


Formula (2)



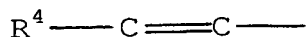
- 5 (wherein in formula (1), each R^1 independently represents formula (3) or (4), and in formula (1) or (2), X^1 and X^2 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and 2 to 30 carbon atoms, provided that X^1 and X^2 may
- 10 be ester-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) as a repeating unit);

Formula (3)



- 15 (wherein R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms);

Formula (4)

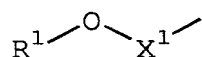


- 20 (wherein R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).

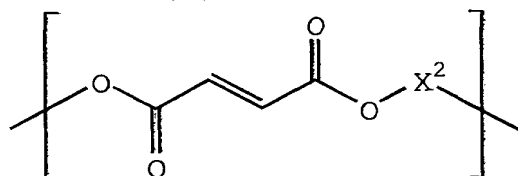
And the present invention (II) is a fumarate derivative having at least one group represented by formula (1) as the terminal groups and having two or more groups represented by formula (2) and/or formula (5) as a

5 repeating unit:

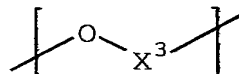
Formula (1)



Formula (2)

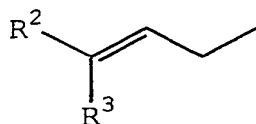


10 Formula (5)



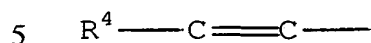
(wherein in formula (1), each R^1 independently represents formula (3) or (4), and in formulae (1), (2) and (5), X^1 , X^2 and X^3 each independently represents an organic residue
 15 derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms, provided that X^1 , X^2 and X^3 may be ester-bonded and/or ether-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and
 20 having a group represented by formula (2) and/or formula (5) as a repeating unit);

Formula (3)



(wherein R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms);

Formula (4)



(wherein R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).

And the present invention (III) is a method for producing the fumarate derivative of the present invention

10 (I) or (II).

Moreover, the present invention (IV) is a polymerizable composition comprising the fumarate derivative of the present invention (I) or (II).

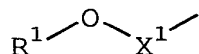
And the present invention (V) is a cured product
15 obtained by curing the polymerizable composition of the present invention (IV).

Preferred Embodiments of the Invention

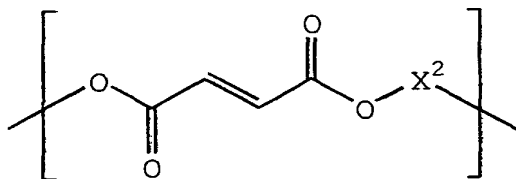
The present invention is described below.

20 At first, the present invention (I) is described. The present invention (I) is a fumarate derivative having at least one group represented by formula (1) as the terminal groups and having two or more groups represented by formula (2) as a repeating unit:

Formula (1)

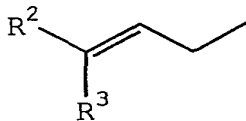


Formula (2)



- 5 (wherein in formula (1), each R^1 independently represents formula (3) or (4), and in formula (1) or (2), X^1 and X^2 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and 2 to 30 carbon atoms, provided that X^1 and X^2 may
- 10 be ester-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) as a repeating unit);

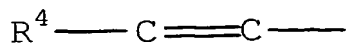
Formula (3)



15

- (wherein R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms);

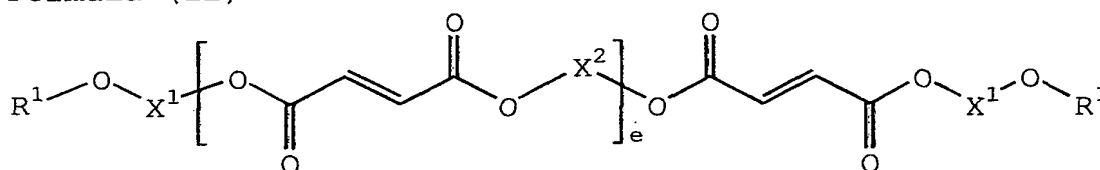
Formula (4)



- 20 (wherein R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).

The present invention (I) has at least one group represented by formula (1) in the terminal groups and containing a fumarate structure represented by formula (2) in two or more repeating unit. Representative examples thereof include a compound represented by formula (12):

Formula (12)



(wherein e represents an integer of 1 to 9).

R^1 in formula (1) according to the present invention represents either formula (3) or formula (4).

In formula (3), R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms. In formula (3), in view of the radical polymerizability, preferred is the case where at least one of R^2 and R^3 is hydrogen atom or a methyl group and the other is at least one of hydrogen atom, a methyl group, an ethyl group, an n-propyl group and an isopropyl group, more preferred is the case where at least one of R^2 and R^3 is hydrogen atom and the other is hydrogen atom or a methyl group, and most preferred is the case where both R^2 and R^3 are hydrogen atoms. With an alkyl group having 4 or more carbon atoms, the polymerizability may disadvantageously decrease.

In formula (4), R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms. In formula (4), in view of the radical polymerizability, R^4 is preferably at least one of hydrogen atom, a methyl group, an ethyl group, an n-propyl group and an isopropyl group, more preferably hydrogen atom or a methyl group. With an alkyl group having 4 or more carbon atoms, the polymerizability may disadvantageously decrease.

X^1 and X^2 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms.

Specific examples of the polyhydric alcohol include alkylene diols such as ethylene glycol, neopentyl glycol, 1,2-propylene glycol, 1,3-propylene glycol, 1,3-butanediol, 1,4-butanediol, 1,6-hexanediol and nonanediol; substituted alkylene glycols such as 1-phenylethylene glycol and 1,2-diphenylethylene glycol; and polyalkylene diols thereof; alicyclic diols such as 1,1-cyclohexanediol, 1,2-cyclohexanediol, 1,3-cyclohexanediol, 1,4-cyclohexanediol, 1,1-cyclohexanedimethanol, 1,2-cyclohexanedimethanol, 1,3-cyclohexanedimethanol, 1,4-cyclohexanedimethanol and tricyclodecanedimethanol; aromatic diols such as bisphenol A, bisphenol F, bisphenol S and benzenedimethanol; and ethylene oxide adducts, propylene oxide adducts,

cyclohexene oxide adducts and styrene oxide adducts of the above polyhydric alcohol.

Also, trihydric alcohols such as trimethylolethane, trimethylolpropane and glycerol; tetrahydric alcohols such as pentaerythritol, diglycerol and ditrimethylolpropane; 5 hexahydric alcohols such as dipentaerythritol and sorbitol; and ethylene oxide adducts, propylene oxide adducts, cyclohexene oxide adducts and styrene oxide adducts of these polyhydric alcohols may be added to an extent not to 10 cause gelation.

Moreover, depending on the kind of a polyhydric alcohol used, there exists a stereoisomer and/or a geometric isomer. For example, when X^2 is an organic residue derived from 1,2-cyclohexanediol, there arises the 15 case to afford cis-cis, cis-trans or trans-trans ester bond and to be an optical isomer as a molecule. In that case, both specific optical isomers concentrated in its ratio with use of optical active column etc., and a mixture thereof without any treatment can be used.

20 Among these, X^1 is preferably an alkylene group having from 2 to 4 carbon atoms, such as ethylene group $-(CH_2)_2-$, 1,3-propylene group $-(CH_2)_3-$ and 1,2-propylene group $(-CH_2-CH(CH_3)-)$; 1,1-cyclohexylene group, 1,2-cyclohexylene group, 1,3-cyclohexylene group, 1,4-cyclohexylene group; or 25 a cycloalkylene having from 6 to 8 carbon atoms, such as

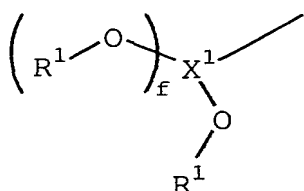
organic residue derived from 1,1-cyclohexanedimethanol,
organic residue derived from 1,2-cyclohexanedimethanol,
organic residue derived from 1,3-cyclohexanedimethanol or
organic residue derived from 1,4-cyclohexanedimethanol,
5 represented by formula $(-\text{CH}_2-\text{C}_6\text{H}_{10}-\text{CH}_2-)$, from the standpoint
that excellent results can be obtained in view of hardness
of the cured product after the polymerization.

Moreover, in order to improve the refractive index of
the cured product, an alkylene diol having phenyl or
10 phenylene group such as bisphenol A, ethylene oxide adducts
of bisphenol A, 1-phenylethylene glycol and 1,2-diphenylene
glycol is preferred.

The number of the repeating units of formula (2) may
be two or more but is preferably from 2 to 10 (e in formula
15 (12) is an integer of 1 to 9). If the number of repeating
units exceeds 10, the viscosity excessively increases and
gelation may disadvantageously occur at the time of
production.

In the case where X^1 is an organic residue derived from
20 a trihydric or greater polyhydric alcohol, X^1 may also have
a branched structure represented by the following formula
(13):

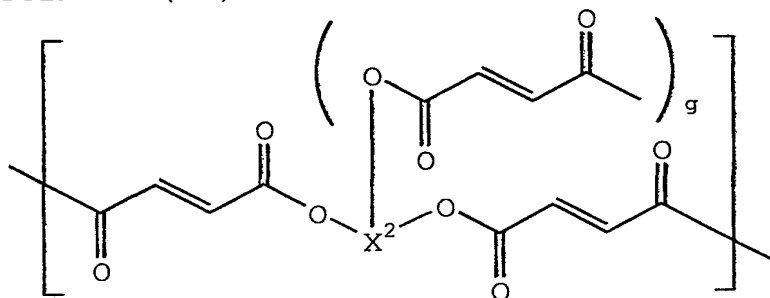
Formula (13)



(wherein f represents an integer of 0 to 4).

In the case where X^2 is an organic residue derived from a trihydric or greater polyhydric alcohol, X^2 may also have a branched structure represented by the following formula (14):

Formula (14)



(wherein g represents an integer of 0 to 4).

R^1 as a polymerizable group at the terminal of formula (1) is by itself poor in the radical polymerizability and curing thereof proceeds in the copolymerization with a fumarate group, therefore, when the molar ratio of R^1 group/fumarate group is close to 1, the cured product can have excellent physical properties. The molar ratio of R^1 group/fumarate group is preferably from 0.2 to 2, more preferably from 0.8 to 1.5.

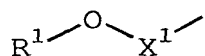
R^1 each independently represents formula (3) or (4). Therefore, the structure of formula (3) and (4) can coexist

in one fumarate derivative molecule of this invention. The terminals having the structure of formula (4) can be produced by the isomerization of all or a part of the structure of formula (3)

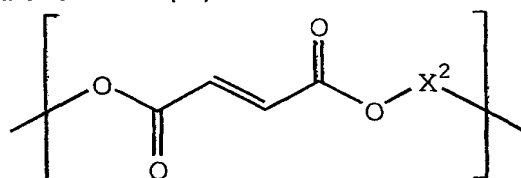
5

Next, the present invention (II) is described below. The present invention (II) is a fumarate derivative having at least one group represented by formula (1) as the terminal groups and having two or more groups represented by formula (2) and/or represented by formula (5) as a repeating unit:

Formula (1)

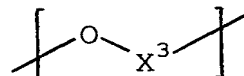


Formula (2)



15

Formula (5)

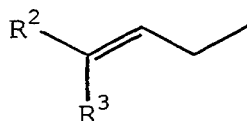


(wherein in formula (1), each R^1 independently represents formula (3) or (4), and in formulae (1), (2) and (5), X^1 , X^2 and X^3 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms, provided that X^1 , X^2 and X^3 may be ester-bonded and/or

20

ether-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) and/or formula (5) as a repeating unit);

5 Formula (3)



(wherein R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms);

Formula (4)

10 $R^4 - C = C -$

(wherein R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).

The fumarate derivative of the present invention (II) has at least one group represented by formula (1) as the terminal groups and contains an ether structure represented by formula (5) as a repeating structure in addition to the fumarate structure represented by formula (2).

In the present invention (II), the terminal group represented by formula (1) and the repeating structure represented by formula (2) are the same as those in the present invention (I).

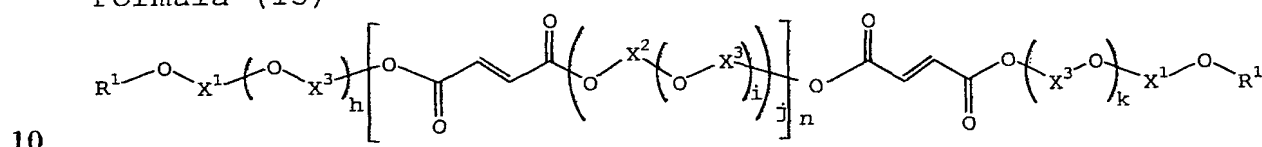
X^3 contained in formula (5) represents an organic residue derived from a polyhydric alcohol having from 2 to

6 hydroxyl groups and having from 2 to 30 carbon atoms similarly to X^1 of formula (1) and X^2 of formula (2).

X^3 is also the same as X^1 of formula (1) and X^2 of formula (2) in the preferred polyhydric alcohol and in the point that X^3 can have a branched structure.

One representative example of the fumarate derivative of the present invention (II) is a compound represented by the following formula (15):

Formula (15)

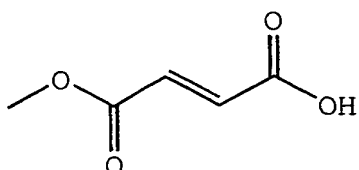


(wherein h , i and k each represents an integer of 0 to 5, j represents an integer of 1 to 5 and n represents an integer of 1 to 9, provided that $h + i + k \geq 1$).

If any one of h , i , j and k exceeds 5, the concentration of the polymerizable double bond decreases to cause reduction in the curability or hardness of the cured product and this is not preferred.

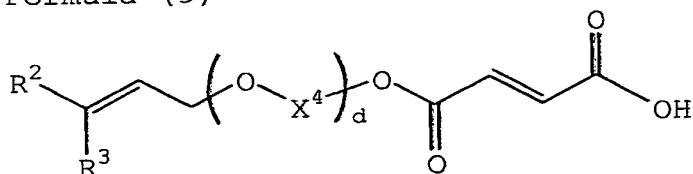
The fumarate derivatives of the present invention (I) and the present invention (II) necessarily have one or more groups represented by formula (1) as a terminal group and may also partially have a carboxyl group represented by formula (8) derived from fumaric acid or a hydroxyl group derived from polyhydric alcohol, as a terminal group.

Formula (8)



Specific examples of the fumarate derivative having a carboxyl group represented by formula (8) derived from fumaric acid as a terminal group includes a compound
 5 represented by formula (9).

Formula (9)



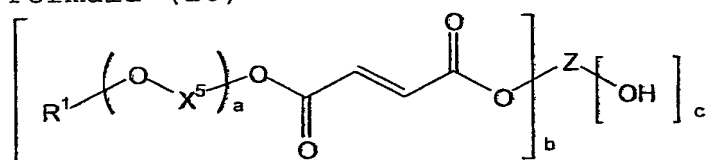
(wherein each X^4 , which is present in the number of d in formula (9), independently represents an alkylene group or
 10 a cycloalkylene group having from 5 to 12 carbon atoms, d represents an integer of 1 to 5, and R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms).

The fumarate derivative represented by formula (9) is
 15 a polymerizable compound having an alkenyl ether group and a carboxylic acid group derived from fumaric acid as the terminal groups and having a fumarate skeleton in the inside thereof. The alkenyl ether group and the fumarate group have high radical copolymerizability. The carboxylic
 20 acid group at the terminal can form an ester bond with

various hydroxyl groups and can synthesize polymerizable ester derivatives having various physical properties.

Specific examples of the compound having a hydroxyl group as a terminal group includes a compound represented
5 by formula (10).

Formula (10)



(wherein Z represents an organic residue derived from a tri-, tetra-, penta- or hexa-hydric alcohol, R^1
10 independently represents formula (3) or formula (4), each X^5 , which is present in the number of a in formula (10), independently represents an alkylene group or a cycloalkylene group having from 5 to 12 carbon atoms, a represents an integer of 1 to 5, b represents an integer of
15 1 to 6, c represents an integer of 0 to 5, and b+c is from 3 to 6);

Formula (10) is a fumarate derivative preferably having either one of the allyl ether group represented by formula (3) and the propenyl ether group represented by
20 formula (4) as a terminal group and at the same time, having a hydroxyl group derived from a polyhydric alcohol as a terminal group. In formula (10), Z represents an organic residue derived from a tri-, tetra-, penta- or hexa-hydric alcohol.

Examples of the polyhydric alcohol as used herein include trihydric alcohols such as trimethylolpropane, trimethylolethane and glycerol; tetrahydric alcohols such as pentaerythritol, ditrimethylolpropane and diglycerol; 5 hexahydric alcohols such as sorbitol and dipentaerythritol; adducts of ethylene oxide or propylene oxide to the hydroxyl group of these tri-, tetra-, penta- and hexahydric alcohols; and mixtures of two or more thereof.

Among these, trimethylolpropane, trimethylolethane, 10 pentaerythritol, ditrimethylolpropane, dipentaerythritol and ethylene oxide adducts of these alcohols, (in these compounds, all hydroxyl groups are primary alcohol) and mixtures of two or more thereof are preferred because of their high reactivity in the esterification reaction.

15

The present invention (III) is described below. The present invention (III) is a method for producing the fumarate derivative of the present invention (I) or (II).

The method for producing a fumarate derivative of the 20 present invention (I) or (II) can be divided into the following two steps A) and B), namely,

A) a step of forming an ester as the main skeleton of the fumarate derivative and forming a repeating unit of the ester, and

B) a step of forming a polymerizable group at terminals represented by formula (4) by isomerization of the group represented by formula (3).

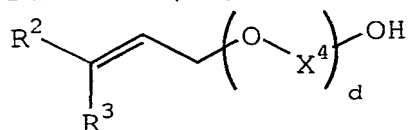
These two steps are not essential in producing the fumarate derivative of the present invention (I) or (II) and only through either one step, the fumarate derivative of the present invention (I) or (II) can be produced.

The step A) in the production method of the fumarate derivative of the present invention (I) or (II) is described below.

The fumarate derivative represented by formula (9) of the present invention (I) can be produced by a method of addition reaction of a maleic anhydride and an alcohol represented by formula (16) to obtain a maleic acid monoester and then isomerizing the ester from maleate into fumarate. In this isomerization reaction, maleate does not necessarily isomerize to fumarate by 100%, and in some cases a mixture of maleate and fumarate is obtained.

In the view point of polymerizability, the formation of fumarate is preferred.

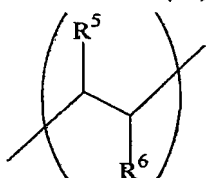
Formula (16)



(wherein X⁴ which exists in number of d in formula (16), each independently represents an alkylene group, a

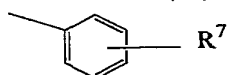
cycloalkylene group having from 5 to 12 carbon atoms or a
alkylene group represented by formula (6), d represents an
integer of 1 to 5, and R^2 and R^3 each independently
represents hydrogen atom or an alkyl group having from 1 to
5 5 carbon atoms).

Formula (6)



(wherein R^5 and R^6 each independently represents hydrogen
atom or formula (7));

10 Formula (7)



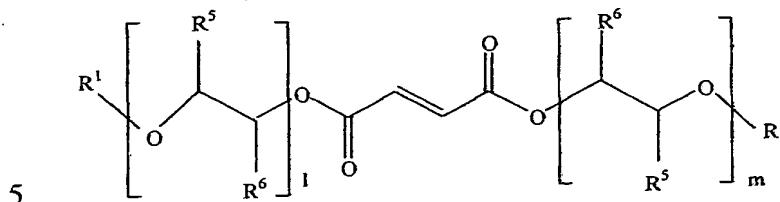
(wherein R^7 represents hydrogen atom or an alkyl group
having from 1 to 3 carbon atoms).

The fumarate derivative represented by formula (10) of
15 the present invention (I), where R^1 is formula (3), can be
produced by an esterification reaction of the fumarate
derivative represented by formula (9) with a polyhydric
alcohol.

And, the fumarate derivative represented by formula
20 (11) of the present invention (I), where R^1 is formula (3),
can be produced by an esterification reaction of a fumarate
derivative represented by formula (9) with an alcohol
represented by formula (16) or an esterification reaction

of an alcohol represented by formula (16) with a fumaric acid, or a transesterification reaction between a dialkyl fumarate and an alcohol represented by formula (16).

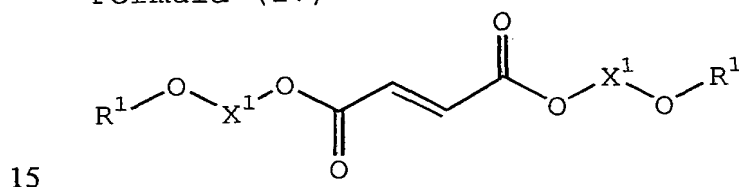
Formula (11)



(wherein, R^1 independently represents formula (3) or formula (4), and l and m each independently represents an integer of 1 to 5);

Furthermore, the fumarate derivative represented by
 10 formula (12) of the present invention (I), where R^1 is formula (3), can be produced by a transesterification reaction between a fumarate derivative represented by formula (17) and a polyhydric alcohol.

Formula (17)

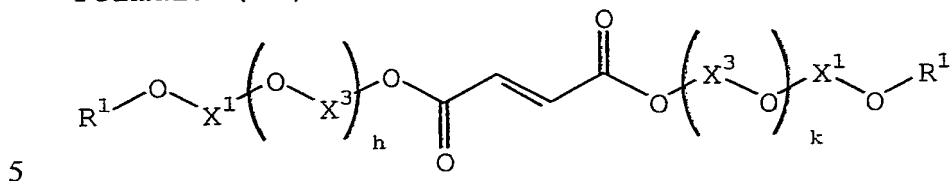


(wherein each R^1 independently represents formula (3) or (4), and X^1 represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms).

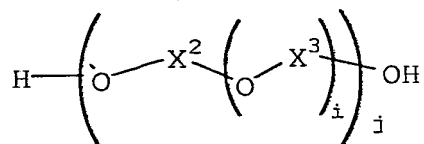
20 The fumarate derivative represented by formula (15) of the present invention (II), where R^1 is formula (3), can be

produced by a transesterification reaction between a fumarate derivative represented by formula (18) and a polyhydric alcohol represented by formula (19):

Formula (18)

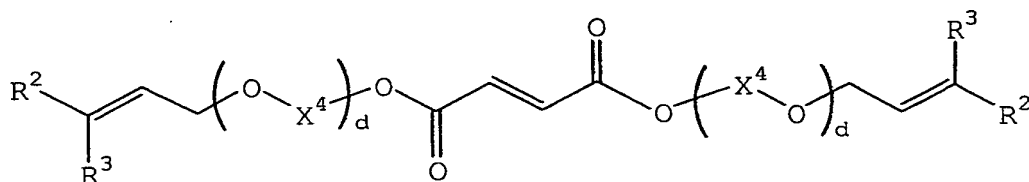


Formula (19)



And, the fumarate derivative represented by formula (20) can be produced by an esterification reaction of the fumarate derivative represented by formula (9) with an alcohol represented by formula (16) or an esterification reaction of an alcohol represented by formula (16) with a fumaric acid.

15 Formula (20)

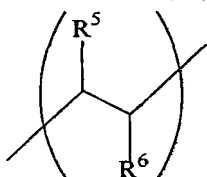


(wherein X^4 which exists in number of d in formula (20), each independently represents an alkylene group, a cycloalkylene group having from 5 to 12 carbon atoms or a

20

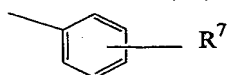
alkylene group represented by formula (6), d represents an integer of 1 to 5, and R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms).

5 Formula (6)



(wherein R^5 and R^6 each independently represents hydrogen atom or formula(7));

Formula (7)



10

(wherein R^7 represents hydrogen atom or an alkyl group having from 1 to 3 carbon atoms).

The method for producing the fumarate derivative
15 represented by formula (9) is described in detail below.
Specific examples of the method for producing the fumarate derivative represented by formula (9) include a method of addition reaction of a maleic anhydride and an alcohol represented by formula (16) to obtain a maleic acid
20 monoester and then isomerizing the ester from maleate to fumarate.

The addition reaction of a maleic anhydride and an alcohol represented by formula (16) can be performed in the

presence or absence of a catalyst. The catalyst is not particularly limited as long as it is a general esterification catalyst but preferred examples thereof include basic catalysts such as triethylamine and N,N-
5 dimethylaminopyridine.

The reaction is performed at a temperature of 20 to 150°C, preferably from 40 to 120°C. If the reaction temperature is less than 20°C, the reaction proceeds slowly and unnecessarily takes a time and this is not preferred,
10 whereas if the reaction temperature exceeds 150°C, the amount of diester produced increases and the yield disadvantageously decreases.

The ratio of the amount charged of the maleic anhydride to the amount charged of the alcohol represented
15 by formula (16) is not particularly limited. The alcohol represented by formula (16) is generally from 0.2 to 10 equivalents in mol, preferably from 0.5 to 5 equivalents in mol, more preferably from 0.9 to 2 equivalents in mol, to 1 mol of the maleic anhydride.

20 If the ratio of the amount charged of the alcohol represented by formula (16) exceeds 10 equivalents in mol, excess alcohol increases, whereas if the ratio is less than 0.2 equivalents in mol, unreacted maleic anhydride increases and this is not preferred in view of
25 profitability.

In this addition reaction, a solvent may be added. Examples of the solvent include aromatic hydrocarbons such as benzene, toluene and xylene, and ethers such as diethyl ether, dimethoxyethane, methoxy ethyl ether,
5 tetrahydrofuran and 1,4-dioxane.

In the alcohol represented by formula (16), R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms, similarly to R^2 and R^3 in formula (3).

10 In the alcohol, R^2 and R^3 both are preferably hydrogen atoms in view of the polymerizability. Specific examples of the alcohol represented by formula (16) include ethylene glycol monoallyl ether, propylene glycol monoallyl ether, 1,3-butylene glycol monoallyl ether, 1,4-butylene glycol
15 monoallyl ether, cyclohexanediol monoallyl ether, cyclohexanedimethanol monoallyl ether, diethylene glycol monoallyl ether, dipropylene glycol monoallyl ether, 2-allyloxy-2-phenylethanol, 2-allyloxy-1-phenylethanol, and 2-allyloxy-1,2-diphenylethanol.

20 The obtained maleic acid monoester can be isomerized into a fumaric acid monoester using a known acidic catalyst such as hydrochloric acid, a basic catalyst such as morpholine, piperidine or diethylamine, or a catalyst such as thiourea, chlorine, bromine, iodine or acid chloride.

The reaction temperature in the isomerization reaction is not particularly limited and is generally from 30 to 200°C, preferably from 50 to 150°C, more preferably from 70 to 120°C. If the reaction temperature exceeds 200°C, the polymerization or decomposition reaction disadvantageously bears higher danger.

In this isomerization reaction, a known hindered phenol-base polymerization inhibitor or a solvent may be used. Examples of the solvent used herein include aromatic hydrocarbons such as benzene, toluene and xylene; ethers such as diethyl ether, dimethoxyethane, methoxy ethyl ether, tetrahydrofuran and 1,4-dioxane; esters such as ethyl acetate and butyl acetate; ketones such as acetone and methyl ethyl ketone.

The fumarate derivative represented by formula (9) obtained as such can be purified by a treatment such as distillation, liquid separation or re-crystallization.

Next, the method for producing the fumarate derivative represented by formula (10) where R^1 is formula (3) is described below.

The fumarate derivative represented by formula (10) where R^1 is formula (3) can be produced by an esterification reaction of the fumarate derivative represented by formula (9) and a polyhydric alcohol. Specific examples of the

esterification reaction include the following three methods:

① a method of esterifying the fumarate derivative represented by formula (9) and a polyhydric alcohol in the presence of an acid catalyst,

② a method of inducing the fumarate derivative represented by formula (9) into an acid halide and then reacting it with a polyhydric alcohol to perform the esterification, and

③ a method of reacting the fumarate derivative represented by formula (9) with a polyhydric alcohol using a condensing agent to perform the esterification.

The method ① is described below.

Examples of the esterification catalyst which can be used in the method ① include known catalysts such as sulfuric acid, p-toluenesulfonic acid, methanesulfonic acid, ion exchange resin, a mixed catalyst of boric acid and sulfuric acid, polyphosphoric acid and Lewis acid (e.g., boron trifluoride etherate).

The reaction can be performed under atmospheric pressure, applied pressure or reduced pressure, for example, at 15 Pa to 1 MPa in terms of an absolute pressure. The reaction temperature is from 20 to 200°C, preferably from 40 to 150°C, and the reaction is performed while distilling off water generated as a by-product. If the reaction

temperature is less than 20°C, the reaction proceeds slowly, whereas if it exceeds 200°C, by-products such as polymerization product may increase.

At the reaction, a solvent may be used. The solvent
5 used is not particularly limited and specific examples thereof include benzene, hexane, cyclohexane, toluene and xylene.

The charging ratio of the fumarate derivative represented by formula (9) to a polyhydric alcohol is not
10 particularly limited but these are preferably charged such that the hydroxyl group (-OH) of the polyhydric alcohol is from 0.2 to 5 equivalents in mol, more preferably from 0.5 to 1.5 equivalents in mol, to the carboxyl group (-COOH) of the fumarate derivative represented by formula (9). If the
15 charging ratio is less than 0.2 equivalents in mol, the residual amount of the fumarate derivative represented by formula (9) is excessively large, whereas if it exceeds 5 equivalents in mol, unreacted hydroxyl group disadvantageously remains.

20 Depending on the reaction conditions, for example, the alcohol corresponding to $R^1-(OX^5)_a-OH$ may be partly eliminated from the ester position of the fumarate derivative represented by formula (10), this alcohol causes an esterification reaction with the carboxyl group of the
25 fumarate derivative represented by formula (9) to produce a

diester monomer of fumaric acid, and the monomer is contained in the product in some cases, however, the product can be used as a polymerizable composition without removing the monomer.

5 After the completion of the esterification reaction, purification may also be performed for removing the impurities or unreacted reactants. The purification may be performed, for example, by dissolving a fumarate derivative in an organic solvent such as benzene, toluene, cyclohexane,
10 diethyl ether, methyl acetate or ethyl acetate, washing the solution with water or alkali, and thereby removing the unreacted fumarate derivative represented by formula (9) or carboxylic acids as by-product, in the form of a salt.

 The purity may also be increased by a method of
15 subjecting the product to decantation or re-precipitation with an organic solvent such as aliphatic hydrocarbons (e.g., hexane, octane), by a method of purifying the product through a column using silica gel or by thin layer chromatography.

20 The method ② is described below.

 The method ② is a method of inducing the fumarate derivative represented by formula (9) into an acid halide and then reacting it with a polyhydric alcohol to perform the esterification.

In the method ②, the method of inducing the fumarate derivative represented by formula (9) into an acid halide is not particularly limited and a known method using thionyl chloride, phosphoryl chloride, phosphorus pentachloride, phosphorus trichloride or phosgene may be used.

Particularly, in the case where thionyl chloride is used, zinc chloride, pyridine, iodine or triethylamine may be used in combination as a catalyst. Also, a mixture of thionyl chloride and dimethylformamide, and a mixture of thionyl chloride and hexamethylphosphoric triamide are known to be a good reagent for synthesizing the acid halide.

By reacting the thus-induced acid halide of the fumarate derivative represented by formula (9) with a polyhydric alcohol using a known method, the fumarate derivative represented by formula (10) of the present invention can be produced.

The method ③ is described below.

The method ③ is a method of reacting the fumarate derivative represented by formula (9) with a polyhydric alcohol using a condensing agent to perform the esterification.

Specific examples of the condensing agent for use in the method ③ include dicyclohexylcarbodiimide, trifluoroacetic anhydride and sulfonyl chloride, however,

the present invention is not limited thereto. Any commonly known condensing agent may be used without any limit.

Among these, a method of using sulfonyl chloride is preferred in view of the easiness to handle. Examples of the case where sulfonyl chloride is used as the condensing agent include a method of adding a base to the fumarate derivative represented by formula (9) in the presence of a solvent, followed by the reaction, adding sulfonyl chloride and finally adding a polyhydric alcohol, followed by the reaction.

Examples of the sulfonyl chloride used here include p-toluenesulfonyl chloride, methanesulfonyl chloride and trifluoromethanesulfonyl chloride.

The charging amounts of the fumarate derivative represented by formula (9) and the sulfonyl chloride are not particularly limited, however, sulfonyl chloride in equivalent or more is generally used. The sulfonyl chloride is preferably charged in an amount of 1 to 2 equivalents in mol to the fumarate derivative represented by formula (9).

The charging ratio of the fumarate derivative represented by formula (9) and a polyhydric alcohol is not particularly limited. These are preferably charged such that the hydroxyl group (-OH) of the polyhydric alcohol is from 0.2 to 2 equivalents in mol, more preferably from 0.4

to 1.2 equivalents in mol, to the carboxyl group (-COOH) of the fumarate derivative represented by formula (9).

The solvent used here is not particularly limited as long as it does not inhibit the reaction. Specific examples thereof include ethers such as tetrahydrofuran and dioxane; aromatic hydrocarbons such as benzene, toluene and xylene; halides such as chloroform, dichloromethane and dichloroethane; dimethylformamide; and dimethylsulfoxide.

Examples of the base include alkali metals such as sodium hydroxide, potassium hydroxide, cesium hydroxide, sodium carbonate, potassium carbonate, cesium carbonate, sodium hydrogencarbonate and potassium hydrogencarbonate.

The amount of the base varies depending on the kind thereof, however, is preferably from 1 to 5 equivalents in mol to the fumarate derivative represented by formula (9).

The reaction temperature is from -20 to 100°C, preferably from 0 to 50°C. If the reaction temperature exceeds 100°C, the side reaction increases, whereas if it is less than -20°C, the reaction may be disadvantageously delayed.

The product obtained can be purified for removing impurities. Examples of the purification method include a method of dissolving the product in an organic solvent such as benzene, toluene, xylene, cyclohexane, methyl acetate, ethyl acetate, diethyl ether, dichloroethane or chloroform,

and then washing the solution with water, alkali or acid; a method of subjecting the product to decantation or re-precipitation with an organic solvent such as aliphatic hydrocarbon (e.g., hexane, octane). The purity may also be enhanced by column purification using silica gel or thin layer chromatography.

The method for producing the fumarate derivative represented by formula (11) of the present invention (I), where R^1 is formula (3), is described below.

The fumarate derivative represented by formula (11) of the present invention (I), where R^1 is formula (3), can be produced by an esterification reaction of the fumarate derivative represented by formula (9) with the alcohol represented by formula (16) or and an esterification reaction of a fumaric acid with the alcohol represented by formula (16).

Specific examples of the esterification reaction are the same with that described in the method for producing the fumarate derivative represented by formula (10) where R^1 is formula (3). A transesterification reaction between a dialkyl fumarate and the alcohol represented by formula (16) is exemplified as the other method.

Namely, the fumarate derivative represented by formula (11) where R^1 is formula (3), can be produced by reacting a

dialkyl fumarate with the alcohol represented by formula (16) in the presence of known transesterification catalyst while removing alcohol generated as a by-product.

Specific examples of the dialkyl fumarate include
5 dimethyl fumarate, diethyl fumarate, di-n-propyl fumarate, di-isopropyl fumarate, di-n-butyl fumarate, di-sec-butyl fumarate and di-t-butyl fumarate. Preferred are dimethyl fumarate, diethyl fumarate, di-n-propyl fumarate and di-isopropyl fumarate because of the easiness of removing the
10 side-produced alcohol.

The transesterification catalyst, which can be used here, is not particularly limited. Specific examples thereof include alkali metals, alkaline earth metals, oxides thereof, oxides and hydroxides of Zn, Sn and Ti,
15 alcoholates, and acetylacetonate complexes.

The reaction temperature is from 80 to 200°C and the reaction may be performed under atmospheric pressure, applied pressure or reduced pressure, for example, at 15 Pa to 1 MPa in terms of the absolute pressure.

20 The fumarate derivative represented by formula (11) may also be obtained by once synthesizing a compound where a part of the fumarate of the fumarate derivative represented by formula (11) is maleate, and isomerizing the compound.

The maleate derivative used for this isomerization reaction can be synthesized with the same method for producing the fumarate derivative represented by formula (11) as above, namely, by an esterification reaction of a maleic acid or a maleic anhydride with the alcohol represented by formula (16).

Specific examples of the esterification reaction are the same as described in the method for producing the fumarate derivative represented by formula (10) where R^1 is formula (3). A transesterification reaction between a dialkyl maleate and the alcohol represented by formula (16) is exemplified as the other method.

The transesterification reaction is the same as described in the method for producing the fumarate derivative represented by formula (11) where R^1 is formula (3), and the maleate derivative can be produced by reacting a dialkyl maleate with the alcohol represented by formula (16) in the presence of known transesterification catalyst while removing alcohol generated as a by-product.

The catalyst for use in the isomerization reaction from maleate to fumarate is preferably a complex of an element such as palladium, rhodium or ruthenium, or a supported catalyst comprising a support having supported thereon such an element. Particularly, in the case of

purifying the fumarate derivative, a supported catalyst is preferably used in view of removal of the catalyst.

The support for use in such a supported catalyst is not particularly limited and a porous substance commonly
5 used as a catalyst may be used. Specific examples thereof include silica, alumina, silica-alumina, zeolite, activated carbon, titania, magnesia and other inorganic compounds.

The amount of the element supported on a support is preferably from 0.05 to 20% by mass, more preferably from 2
10 to 10% by mass, based on the entire amount of the catalyst. If the supported amount is less than 0.05% by mass, the reaction takes a time, whereas if it exceeds 20% by mass, the element not participating in the isomerization reaction disadvantageously increases.

15 The thus-obtained supported catalyst is preferably used in an amount of 0.01 to 50% by mass, more preferably from 1 to 30% by mass, based on the maleate derivative. If the amount used is less than 0.01% by mass, the reaction takes a time, whereas if it exceeds 50% by mass, the
20 catalyst not participating in the isomerization reaction disadvantageously increases. The isomerization catalyst can be used individually or in combination of two or more thereof.

The temperature at the isomerization reaction is not
25 particularly limited. The isomerization reaction

temperature is generally from 30 to 200°C, preferably from 60 to 180°C, more preferably from 80 to 160°C. If the reaction temperature is less than 30°C, the reaction proceeds slowly, whereas if it exceeds 200°C, polymerization
5 may occur during the isomerization reaction and this is not preferred.

In the present invention, the isomerization reaction may also be performed in a solvent. Examples of the solvent which can be used include aromatic hydrocarbons such as
10 benzene, toluene and xylene; ethers such as diethyl ether, dimethoxyethane, methoxyethyl ether, tetrahydrofuran and 1,4-dioxane; esters such as ethyl acetate and butyl acetate; ketones such as acetone and methyl ethyl ketone; and alcohols such as methanol, ethanol and isopropanol. In
15 the case of using a solvent, these solvents may be used in combination of two or more thereof.

In the present invention, the isomerization reaction may be performed under atmospheric pressure or applied pressure, for example, at a pressure of 1 KPa to 1 MPa.

20 During the transesterification reaction and the isomerization reaction, a polymerization inhibitor may also be added for preventing occurrence of polymerization.

Examples of the polymerization inhibitor include quinones such as p-benzoquinone, naphthoquinone and 2,5-
25 diphenyl-p-benzoquinone; polyhydric phenols such as

hydroquinone, p-tert-butylcatechol and 2,5-di-tert-butylhydroquinone; and phenols such as hydroquinone monomethyl ether, di-tert-butyl paracresol and α -naphthol.

5 The method for producing the fumarate derivative represented by formula (12) of the present invention (I), where R^1 is formula (3), is described below.

 The fumarate derivative represented by formula (12) where R^1 is formula (3) can be produced by a
10 transesterification reaction between the fumarate derivative represented by formula (17) and the polyhydric alcohol. Namely, the fumarate derivative represented by formula (12) where R^1 is formula (3), can be produced by reacting the fumarate derivative represented by formula
15 (17) with the polyhydric alcohol in the presence of known transesterification catalyst while removing alcohol generated as a by-product.

 Specific examples of the transesterification reaction are the same as described in the method for producing the
20 fumarate derivative represented by formula (11) where R^1 is formula (3).

 In the case of this reaction, the fumarate derivative represented by formula (17) where R^1 is formula (3) may remain in the product depending on the charged ratio to the

polyhydric alcohol, however, the product can be used without removing it.

The fumarate derivative represented by formula (12) may also be obtained by once synthesizing a compound where
5 a part of the fumarate of the fumarate derivative represented by formula (12) is maleate, and isomerizing the compound.

The maleate derivative used for this isomerization reaction can be synthesized with the same method for
10 producing the fumarate derivative represented by formula (11) as above, namely, by a transesterification reaction between the maleate derivative corresponding to the fumarate derivative represented by formula (17) and the polyhydric alcohol.

15 The isomerization reaction from maleate to fumarate is also the same with the method for producing the fumarate derivative represented by formula (11).

The method for producing the fumarate derivative
20 represented by formula (15) of the present invention (II), where R^1 is formula (3), is described below.

The fumarate derivative represented by formula (15) where R^1 is formula (3) can be produced by a transesterification reaction between the fumarate

derivative represented by formula (18) and the polyhydric alcohol represented by formula (19).

To speak more specifically, the fumarate derivative represented by formula (18) can be produced by performing
5 an addition reaction of an ethylene glycol allyl ether or a propylene glycol allyl ether corresponding to R^1-O-X^1-OH with an epoxy compound having the X^3 unit, such as ethylene oxide, propylene oxide, cyclohexene oxide or styrene oxide to synthesize a corresponding alcohol, and then an
10 esterification reaction with a fumaric acid or a transesterification reaction with a dialkyl fumarate.

The polyhydric alcohol having ether-bond as represented by formula (19), for example, can be produced by an addition reaction of an alcohol such as ethylene
15 glycol or propylene glycol with an epoxy compound such as ethylene oxide, propylene oxide, cyclohexene oxide or styrene oxide.

In the forgoing pages, the step A) of forming an ester as the main skeleton of the fumarate derivative and forming
20 a repeating unit of the ester is described.

The step B) of forming a polymerizable group at the terminal by isomerization is described below.

The fumarate derivative represented by formula (10) of
25 the present invention (I), where R^1 is formula (4) and the

fumarate derivative represented by formula (11) of the present invention (I), where R^1 is formula (4), can be produced by a method of isomerizing the terminal group of the above-described fumarate derivative represented by formula (10), where R^1 is formula (3) and the fumarate derivative represented by formula (11), where R^1 is formula (3), respectively.

Also, the fumarate derivative represented by formula (12) of the present invention (I), where R^1 is formula (4) and the fumarate derivative represented by formula (15) of the present invention (II), where R^1 is formula (4), can be produced by isomerizing the corresponding fumarate derivatives, where R^1 is formula (3).

* The isomerization reaction is described below.

The isomerization reaction from formula (3) to formula (4) can be performed using a known complex of an element such as palladium, rhodium or ruthenium, or using a supported catalyst comprising a support having supported thereon such an element.

The support for use in the supported catalyst is not particularly limited and a porous substance generally used as the support may be used. Specific examples thereof include silica, alumina, silica-alumina, zeolite, activated carbon, titania, magnesia and other inorganic compounds.

The amount of the element supported on a support is preferably from 0.05 to 20% by mass, more preferably from 2 to 10% by mass, based on the entire amount of the catalyst. If the amount of the element supported is less than 0.05% by mass, the reaction takes a time, whereas if it exceeds 20% by mass, the element not participating in the isomerization reaction disadvantageously increases.

The thus-obtained supported catalyst is preferably used in an amount of 0.01 to 50% by mass, more preferably from 1 to 30% by mass, based on the fumarate derivative represented by formula (10), (11), (12) or (15) containing formula (3). If the amount of the catalyst is less than 0.01% by mass, the reaction takes a time, whereas if it exceeds 50% by mass, the catalyst not participating in the isomerization reaction disadvantageously increases. The isomerization reaction catalyst may be used individually or in combination of two or more thereof.

In the isomerization reaction, the reaction temperature is not particularly limited and is generally from 30 to 200°C, preferably from 60 to 180°C, more preferably from 80 to 160°C. If the reaction temperature is less than 30°C, the reaction takes a time, whereas if it exceeds 200°C, polymerization may occur during the isomerization reaction and this is not preferred.

In the present invention, the isomerization reaction may be performed in a solvent. Examples of the solvent which can be used include aromatic hydrocarbons such as benzene, toluene and xylene; ethers such as diethyl ether, dimethoxyethane, methoxyethyl ether, tetrahydrofuran and 1,4-dioxane; esters such as ethyl acetate and butyl acetate; ketones such as acetone and methyl ethyl ketone; alcohols such as methanol, ethanol and isopropanol. In the case of using a solvent, these solvents may be used in combination of two or more thereof.

In the present invention, the isomerization reaction may be performed under atmospheric pressure or applied pressure, for example, at a pressure of 1 KPa to 1 MPa.

In order to prevent occurrence of polymerization during the isomerization reaction, a polymerization inhibitor may also be added. Examples of the polymerization inhibitor include quinones such as p-benzoquinone, naphthoquinone and 2,5-diphenyl-p-benzoquinone; polyhydric phenols such as hydroquinone, p-tert-butylcatechol and 2,5-di-tert-butylhydroquinone; and phenols such as hydroquinone monomethyl ether, di-tert-butyl paracresol and α -naphthol.

The present invention (IV) is described below.

The present invention (IV) is a polymerizable composition comprising the fumarate derivative of the present invention (I) or (II).

The polymerizable composition of the present invention
5 (IV) may contain, if desired, a compound having radical polymerizability or a radical polymerization initiator in addition to the fumarate derivative of the present invention (I) or (II).

Examples of the radical polymerizable compound include
10 unsaturated polyester, oligomer having (meth)acrylate group, and radical polymerizable monomer.

The unsaturated polyester is obtained by a polycondensation reaction of an α,β -unsaturated polybasic acid or an acid anhydride with a saturated polybasic acid
15 and a polyhydric alcohol.

Examples of the α,β -unsaturated polybasic acid include maleic acid, fumaric acid, itaconic acid, maleic anhydride and itaconic anhydride. Examples of the saturated polybasic acid used in combination as an acid component include
20 saturated aliphatic dicarboxylic acids such as succinic acid, adipic acid and sebacic acid; aromatic polycarboxylic acids such as phthalic anhydride, isophthalic acid, terephthalic acid, trimellitic acid, pyromellitic anhydride and 2,6-naphthalene dicarboxylic acid; and alicyclic
25 dicarboxylic acids such as endic anhydride, 1,2-

cyclohexanedicarboxylic acid, hexahydrophthalic anhydride and 1,4-cyclohexanedicarboxylic acid. Examples of the polyhydric alcohol include aliphatic diols such as ethylene glycol, diethylene glycol, 1,2-propanediol, 1,3-propanediol, 5 dipropylene glycol, 1,3-butanediol, 1,4-butanediol, neopentyl glycol, 2-methyl-1,3-propanediol, 3-methyl-1,5-pentanediol, 1,6-hexanediol, 1,6-nonanediol and 1,9-nonanediol; alicyclic diols such as 1,4-cyclohexanedimethanol, tricyclodecanedimethanol and 10 hydrogenated bisphenol A; aromatic diols such as ethylene oxide or propylene oxide adducts of bisphenol A; and trihydric or greater polyhydric alcohols such as glycerol, trimethylolpropane, trimethylolethane, pentaerythritol, sorbitol and dipentaerythritol.

15 Other examples of the unsaturated polyester include those obtained by a transesterification reaction of the above-described saturated polybasic acid with a dialkyl ester of the unsaturated polybasic acid and the polyhydric alcohol. In this case, the alkyl group is usually a methyl 20 group, an ethyl group, a propyl group or a butyl group.

The (meth)acrylate-base compound for use in the present invention is a compound having two or more (meth)acryloyl groups in the structure and specifically, can be obtained by a reaction of a urethane (meth)acrylate,

a polyhydric alcohol, a polybasic acid or an anhydride thereof, and a (meth)acrylic acid.

Specific examples thereof include polyester (meth)acrylates, polyether (meth)acrylates obtained by
5 reacting a polyhydric alcohol resulting from addition of ethylene oxide or propylene oxide to a hydroxyl group-containing compound with a (meth)acrylic acid, epoxy (meth)acrylates obtained by reacting an epoxy compound with a (meth)acrylic acid or a (meth)acrylate having a carboxyl
10 group, polyfunctional (meth)acrylates such as ethylene glycol di(meth)acrylate, diethylene glycol di(meth)acrylate, neopentyl glycol di(meth)acrylate, glycerol di(meth)acrylate, trimethylolethane tri(meth)acrylate, trimethylolpropane tri(meth)acrylate, pentaerythritol
15 tri(meth)acrylate, pentaerythritol tetra(meth)acrylate and dipentaerythritol hexa(meth)acrylate, and silicon (meth)acrylates having a siloxane group and a (meth)acryloyl group.

The urethane (meth)acrylate for use in the present
20 invention is known and can be obtained by reacting a polyhydric alcohol, a polyisocyanate and a hydroxyethyl (meth)acrylate or hydroxypropyl (meth)acrylate. Examples of the polyhydric alcohol include those described above for the polyhydric alcohol of the unsaturated polyester.
25 Examples of the polyisocyanate include toluene diisocyanate,

4,4'-diphenylmethane isocyanate, xylene diisocyanate, hexamethylene diisocyanate and isophorone diisocyanate.

Examples of the polybasic acid and the polyhydric alcohol used as starting materials of the polyester (meth)acrylate or polyether (meth)acrylate for use in the present invention include those described above with respect to the unsaturated polyester.

Known examples of the epoxy compound used as a starting material of the epoxy (meth)acrylate for use in the present invention include epoxy resin-base compounds such as glycidyl ether of bisphenols (e.g., bisphenol A, bisphenol S, bisphenol F) and novolak .

The radical polymerizable monomer for use in the present invention has a double bond as a polymerizable group. Specific examples thereof include monofunctional (meth)acrylates such as methyl (meth)acrylate, ethyl (meth)acrylate, butyl (meth)acrylate, 2-ethylhexyl (meth)acrylate, phenyl (meth)acrylate, benzyl (meth)acrylate and isobornyl (meth)acrylate; aromatic vinyl compounds such as styrene, α -styrene, methoxy styrene and divinylbenzene; vinyl esters of aliphatic carboxylic acid, such as vinyl acetate, vinyl propionate, vinyl butyrate, vinyl pivalate, vinyl stearate and vinyl caproate; alicyclic vinyl esters such as vinyl ester of cyclohexanecarboxylic acid ; vinyl ester of aromatic acid

such as vinyl benzoate and vinyl t-butyl benzoate;
hydroxyalkyl vinyl esters such as hydroxyethyl vinyl ester,
hydroxypropyl vinyl ester and hydroxybutyl vinyl ester;
allyl compounds such as diallyl phthalate, diallyl
5 isophthalate, diallyl terephthalate, diallyl maleate,
diallyl fumarate, diallyl itaconate, triallyl trimellitate,
triallyl cyanurate, triallyl isocyanurate, diallyl
carbonate, diethylene glycol bisallyl carbonate,
trimethylol propane diallyl ether and pentaerythritol
10 triallyl ether; maleimides such as N-methylmaleimide, N-
cyclohexylmaleimide, N-phenylmaleimide, N-laurylmaleimide,
N-2-methylphenylmaleimide, N-2-chlorophenylmaleimide, N-2-
methoxyphenylmaleimide, N,N-4,4'-diphenylmethane bismale-
imide; unsaturated dibasic acids and derivatives thereof,
15 such as maleic acid, fumaric acid, maleic anhydride,
dimethyl maleate, diethyl maleate, dimethyl fumarate,
diethyl fumarate, dimethyl itaconate and diethyl itaconate;
and the fumarate derivatives represented by formulae (17)
and (18).

20 Particularly, when the fumarate derivative represented
by formula (17) or (18) is used and blended, the
polymerizable composition of the present invention (IV) is
not prone to curing inhibition by oxygen and can have good
surface curability. These radical polymerizable monomers

can be used individually or in combination of two or more thereof.

The amount of the fumarate derivative of the present invention (I) or (II) used in the polymerizable composition of the present invention (IV) is from 1 to 99% by mass, preferably from 5 to 80% by mass, in the curable composition. In particular, when the amount used is 5% by mass or more, the polymerizable composition is scarcely affected by the curing inhibition due to oxygen and can be prevented from occurrence of surface stickiness.

The radical polymerization initiator which can be used for the polymerizable composition of the present invention (IV) may be any radical polymerization initiator as long as it can generate a radical, for example, by heat, ultraviolet ray, electron beam or radiation.

Examples of the radical polymerization initiator which can be used in the radical polymerization by heat include azo-base compounds such as 2,2'-azobisisobutyronitrile and 2,2'-azobisisovaleronitrile; ketone peroxides such as methyl ethyl ketone peroxide, methyl isobutyl ketone peroxide and cyclohexanone peroxide; diacyl peroxides such as benzoyl peroxide, decanoyl peroxide and lauroyl peroxide; dialkyl peroxides such as dicumyl peroxide, tert-butylcumyl peroxide and di-tert-butyl peroxide; peroxy ketals such as 1,1-bis(tert-butylperoxy)3,3,5-trimethyl

cyclohexane, 1,1-di-tert-butylperoxy cyclohexane and 2,2-di(tert-butylperoxy)butane; alkylperoxy esters such as tert-butylperoxy pivalate, tert-butylperoxy-2-ethyl hexanoate, tert-butylperoxy isobutylate, di-tert-butylperoxy hexahydroterephthalate, di-tert-butylperoxy azelate, tert-butylperoxy-3,5,5-trimethyl hexanoate, tert-butylperoxy acetate, tert-butylperoxy benzoate, di-tert-butylperoxy trimethyladipate, tert-butylperoxy 2-ethylhexanoate and tert-hexylperoxy 2-ethylhexanoate; and
10 percarbonates such as diisopropylperoxy dicarbonate, di-sec-butylperoxy dicarbonate and tert-butylperoxy isopropylcarbonate.

In the film formation such as coating by heat, it is also possible to cause self-crosslinking without using a
15 radical polymerization initiator.

Examples of the radical polymerization initiator which can be used for the polymerization by ultraviolet ray or electron beam include acetophenone derivatives such as acetophenone, 2,2-dimethoxy-2-phenylacetophenone, diethoxy-
20 acetophenone, 1-hydroxy-cyclohexyl-phenyl ketone, 2-methyl-1-[4-(methylthio)phenyl]-2-morpholinopropanone-1, 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 and 2-hydroxy-2-methyl-1-phenyl-propan-1-one; benzophenone derivatives such as benzophenone, 4,4'-
25 bis(dimethylamino)benzophenone, 4-

trimethylsilylbenzophenone and 4-benzoyl-4'-methyl-
diphenylsulfide; benzoin derivatives such as benzoin,
benzoin ethyl ether, benzoin propyl ether, benzoin isobutyl
ether and benzoin isopropyl ether; methyl phenyl
5 glyoxylate; benzoin dimethyl ketal; and 2,4,6-
trimethylbenzoyldiphenylphosphine oxide.

The amount of the polymerization initiator used is
from 0.01 to 15% by mass, preferably from 0.1 to 10% by
mass, based on the weight of the polymerizable composition
10 of the present invention (IV).

In the case of polymerizing the polymerizable
composition of the present invention, various additives may
be added according to the use end. Examples of the
additives which can be used in combination include
15 ultraviolet absorbent, antioxidant, coloring agent,
lubricant, antistatic agent and inorganic filler such as
silica, alumina and aluminum hydroxide.

The polymerizable composition of the present invention
(IV) can be cured by a curing method using ultraviolet ray,
20 electron beam or heat, such as coating by means of roll
coater or spin coater, cast formation or photoformation.

Depending on the curing method, when the viscosity of
the polymerizable composition of the present invention must
be lowered, a solvent may be used. Examples of the solvent,
25 which can be used, include aromatic hydrocarbons such as

toluene and xylene; acetic acid esters such as methyl acetate, ethyl acetate, propyl acetate and butyl acetate; ketones such as acetone, methyl ethyl ketone and methyl isobutyl ketone; ethers such as tetrahydrofuran and dioxane; and alcohols such as ethyl alcohol, (iso)propyl alcohol and butyl alcohol.

The present invention (V) is described below. The present invention (V) is a cured product obtained by curing the polymerizable composition of the present invention (IV).

The cured product of the present invention (V) can be used over a wide range in the field of curable resin, for example, coating materials such as wood coating, film coating, metal coating, plastic coating, inorganic coating, hard coating, optical fiber coating and gel coating agent; painting materials such as coating or printing ink; optical materials such as photoformation material, optical disk, spectacle lens and prism; adhesive; photoresist; sealant; and molding materials. The cured product of the present invention (V) is useful particularly as a coating material for forming a thin film, which is prone to inhibition by oxygen. The substrate subjected to the coating is not particularly limited. Specific examples thereof include metal, glass and plastic.

The resin obtained by curing the polymerizable composition of the present invention has a high crosslinking density and therefore, a cured product having a high surface hardness can be obtained. In particular, a
5 cured resin of the fumarate derivative having a tri-, tetra-, penta- or hexa-hydric alcohol in the skeleton, represented by formula (10), has a surface hardness as high as 4H to 8H in terms of the pencil hardness (JIS K-5400) and therefore, can be optimally used in the field where
10 abrasion resistance or scratch resistance is required.

Examples

The present invention is described in greater detail below by referring to the Examples, however, the present
15 invention should not be construed as being limited to these Examples as long as the spirit of the present invention is observed.

In the measurements of various data, the following instruments were used.

20 (Instruments Used)

¹H-NMR

Model of instrument used: JEOL EX-400 (400 MHz)

A sample was dissolved in chloroform deuteride and measured using tetramethylsilane as the internal standard
25 substance, and a chemical shift was calculated.

FT-IR

Model of instrument used:

Spectrum GX manufactured by Perkin-Elmer

The measurement was performed by a liquid film method
5 using KBr plate.

GPC

Model of instrument used:

pump: Shodex DS-4, UV detector: Waters 484,

RI detector: Shodex RI SE-61

10 Column used:

Shodex K-G+K-801 (in Example 1, K-802 was added)

Measuring conditions:

eluent: chloroform, flow rate: 1 ml/min.,

column temperature: 40°C, detection: UV 254 nm

15 GC (monomer analysis)

Model of instrument used:

GC-14B (manufactured by Shimadzu Seisakusho)

Column used:

DB-23, 0.25 μ \times 30 m (manufactured by J & W)

20 Carrier gas: nitrogen, 1 ml/min.

Split ratio: 1:50

Septum purge: 10 ml/min.

Detector: FID

Injection temperature: 230°C

25 Detector temperature: 230°C

Temperature program:

40°C (10 min.) → (10°C/min.) → 200°C

UV irradiation apparatus

Model of instrument used:

5 TOSCURE 401 (manufactured by Toshiba K.K.),

Light source: mercury lamp,

Irradiation intensity:

irradiation distance: 100 mm - 70 mW/cm²

Melting point

10 Model of instrument used:

MP-500D (manufactured by Yanaco)

Refractive index

Model of instrument used:

Abbé's refractometer IT (manufactured by Atago)

15 Refractive index (n_D) was measured with use of the
above instrument using α -bromonaphthalene as a
contacting liquid.

Temperature: 25°C

20 (Example 1)

Into a 1 L-volume flask equipped with a distillation
unit, 312 g of bis(2-allyloxyethyl) maleate, 135 g of
ethylene oxide 2-mol adduct of bisphenol A, 0.4 g of
dibutyltin oxide and 0.12 g of tetrakis[methylene-3-(3,5-

25 di-tert-butyl-4-hydroxyphenyl)propionate]methane ("IRGANOX

1010", trade name, produced by Chiba Specialty Chemicals) as a polymerization inhibitor were charged. While gradually reducing the pressure inside of the reaction system, the mixture was heated at 160°C and ethylene glycol monoallyl ether generated as a by-product was distilled off. Finally, the pressure was reduced to about 400 Pa and a nearly theoretical amount of ethylene glycol monoallyl ether was distilled off.

After cooling the reaction solution to a room temperature, 385 g of the product was taken out. ¹H-NMR and IR of the product obtained were measured and this product was identified as a condensate of bis(2-allyloxyethyl) maleate with ethylene oxide 2-mol adduct of bisphenol A.

By the GC analysis, the product was found to contain 30.3% of bis(2-allyloxyethyl) maleate.

¹H-NMR

δ(ppm): 7.13-7.11 (m, Ph), 6.81-6.78 (m, Ph), 6.29 (s, -OCOCH=CHCOO-), 5.95-5.84 (m, CH₂=CH-CH₂-), 5.31-5.25 (m, CH₂=CH-CH₂-), 5.21-5.17 (m, CH₂=CH-CH₂-), 4.52-3.64 (m, -O-CH₂-CH₂-COO-, CH₂=CH-CH₂-, -O-CH₂-CH₂-COO-, Ph-O-CH₂-CH₂-OCO-C=C-), 1.63 (s, Ph-C(Me)₂-Ph), 1.62 (Ph-C(Me)₂-Ph).

IR

ν(CO)=1,733 cm⁻¹, ν(allyl C=C, maleate C=C)=1,647 cm⁻¹

62.4 g of the mixture obtained, 60 ml of toluene, 60ml of 1-propanol and 6.2 g of Ru-C supported in an amount of 5% by mass were charged and after purging with nitrogen, the temperature was elevated to 150°C. Subsequently, the mixture was stirred under heating at the same temperature for 10 hours. After cooling, the catalyst was separated by filtration from the reaction solution and the solvent was distilled off under reduced pressure from the filtrate, as a result, 59.2 g of a highly viscous yellow liquid was obtained. By NMR, the isomerization ratio from the double bond of maleic acid residue ($\delta=6.29$ ppm) to the double bond of fumaric acid residue ($\delta=6.93$ to 6.86ppm) was 100%.

The area percentage in the chart of analysis results by GPC of the product obtained is shown in Table 1 with respect to the condensation degree n (the number of repeating units) of the product.

Table 1

Condensation degree n	1	2	3	4	≥ 5
Composition (area %)	30.3	29.0	23.1	13.0	4.6

20

(Example 2)

Into a 3 L-volume glass flask, 500 g of maleic anhydride, 573 g of ethylene glycol monoallyl ether and

0.05 g of hydroquinone monomethyl ether were charged. The mixture was stirred under heating at 50°C for 24 hours in a nitrogen atmosphere. To the reactant obtained, 1 kg of 1,4-dioxane, 10 g of concentrated hydrochloric acid and 0.1g of hydroquinone monomethyl ether were added and the mixture was stirred under heating at 100°C for 1 hour. Thereafter, 1,4-dioxane was distilled off under reduced pressure and to the reactant, 1 kg of toluene and 1 kg of water were added and liquid-separated. Toluene was distilled off under reduced pressure from the organic layer, as a result, 1,020 g of a pale yellow liquid was obtained. From the analyses by NMR and FT-IR, the product was identified as mono-2-allyloxyethyl fumarate.

¹H-NMR

δ(ppm): 10.44 (br.s, 1H, -COOH), 7.30-6.83 (m, 2H, -OCOCH=CHCOO-), 5.92-5.88 (m, 1H, CH₂=CH-CH₂-), 5.32-5.21 (m, 2H, CH₂=CH-CH₂-), 4.37 (br.s, 2H, -O-CH₂-CH₂-COO-), 4.07 (br.s, 2H, CH₂=CH-CH₂-), 3.73 (br.s, 2H, -O-CH₂-CH₂-COO-).

IR

ν(OH)=3,300-2,500 cm⁻¹, ν(CO)=1,727 cm⁻¹,
ν(allyl C=C)= 1,647 cm⁻¹

(Example 3)

Into a 500 ml-volume glass flask equipped with a stirring unit, a thermometer, a condenser and distilling receiver with stopcock, 154 g of mono-2-allyloxyethyl fumarate obtained in Example 2, 21.8 g of pentaerythritol, 5 200 ml of benzene and 0.25 g of p-toluenesulfonic acid were charged. The mixture was stirred under heating in an oil bath, the reaction temperature was elevated to 80°C and the reaction was continued while distilling off the water generated as a by-product with the progress of the reaction. 10 When the amount of water distilled off reached the theoretical amount, the reaction was finished and the reaction solution was cooled. This reaction solution was transferred to a separatory funnel, 300 ml of benzene was added thereto, and the separation was performed using an 15 aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was concentrated under reduced pressure to obtain 120 g of a product.

¹H-NMR, FT-IR, GC and GPC of the product were measured and this product was identified as a composition containing 20 a condensate of pentaerythritol with mono-2-allyloxyethyl fumarate, and 43% (by GC) of bis(2-allyloxyethyl) fumarate monomer.

IR

$\nu(\text{CO})=1,727 \text{ cm}^{-1}$, $\nu(\text{allyl C=C})=1,647 \text{ cm}^{-1}$

(Example 4)

Into a 500 ml-volume glass flask equipped with a stirring unit, a thermometer, a condenser and distilling receiver with stopcock, 152 g of mono-2-allyloxyethyl fumarate obtained in Example 2, 21.5 g of trimethylol propane, 200 ml of benzene and 0.25 g of p-toluenesulfonic acid were charged. The mixture was stirred under heating in an oil bath, the reaction temperature was elevated to 80°C, and the reaction was continued while distilling off the water generated as a by-product with the progress of the reaction. When the amount of water distilled off reached the theoretical amount, the reaction was finished and the reaction solution was cooled. This reaction solution was transferred to a separatory funnel, 300 ml of benzene was added thereto, and the separation was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was concentrated under reduced pressure to obtain 118 g of a product.

¹H-NMR, FT-IR, GC and GPC of the product were measured and this product was identified as a composition containing a condensate of trimethylol propane with mono-2-allyloxyethyl fumarate, and 30% (by GC) of bis(2-allyloxyethyl) fumarate monomer.

IR

$\nu(\text{CO})=1,727 \text{ cm}^{-1}$, $\nu(\text{allyl C=C})=1,647 \text{ cm}^{-1}$

(Example 5)

Into a 3 L-volume glass flask, 500.7 g of mono-2-allyloxyethyl fumarate obtained in Example 2 and 1.8 kg of tetrahydrofuran (THF) were charged. The inside of the reaction system was purged with nitrogen and then 345.5 g of potassium carbonate was added. After the completion of heat generation, the mixture was stirred for 1 hour and the reaction solution was cooled with ice water. Separately, a THF solution was prepared by dissolving 524.3 g of p-toluenesulfonyl chloride in 200 g of THF. When the temperature of the reaction solution reached 10°C or less, the prepared p-toluenesulfonyl chloride/THF solution was added thereto and stirred for 30 minutes. Thereafter, 70.9 g of pentaerythritol and 691.1 g of potassium carbonate were added and stirred. After the completion of heat generation, the ice water was removed and the reaction solution was returned to a room temperature and further stirred for 2 hours.

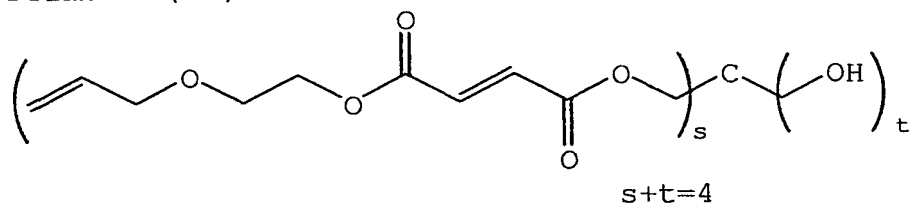
Then, the reaction solution was concentrated, the concentrate was transferred to a separatory funnel, 2 kg of ethyl acetate was added, and the separation washing was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was concentrated under reduced pressure to obtain 240 g of a

product. $^1\text{H-NMR}$, FT-IR and GPC of the product were measured and this product was identified as a condensate of pentaerythritol with mono-2-allyloxyethyl fumarate, represented by formula (21).

5 IR

$$\nu(\text{CO})=1,727 \text{ cm}^{-1}, \nu(\text{allyl C=C})=1,647 \text{ cm}^{-1}$$

Formula (21)



The area percentage in the chart of analysis results
 10 by GPC of the product obtained is shown in Table 2 with respect to the value of s in formula (21).

Table 2

Value of s	4	3	$2 \geq$
Compositional ratio (area % by GPC)	88.3	2.2	9.5

The mixture obtained above was subjected to thin layer
 15 chromatography ("Pre-coated TLC Plates SILICA GEL 60 F-254", produced by MERCK) in which silica was supported, using ethyl acetate/hexane=1/2 as the developer to isolate compounds having a value of s of 4 or 3. These compounds were measured by NMR and the above-described mixture was
 20 re-identified.

$s=4$

^1H -NMR

δ (ppm) 6.92 (d, 4H, $J=15.6\text{Hz}$, $-\text{OCOCH}=\text{CHCOO}-$), 6.85 (d, 4H, $J=15.6\text{Hz}$, $-\text{OCOCH}=\text{CHCOO}-$), 5.96-5.86 (m, 4H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 5.30 (d, 4H, $J=17.3\text{Hz}$, $J=1.47\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 5.22 (dd, 4H, $J=10.5\text{Hz}$, $J=1.47\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 4.38 (t, 8H, $J=4.6\text{Hz}$, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{COO}-$), 4.34 (s, 8H, $\text{C}-\text{CH}_2-$), 4.04 (d, 8H, $J=5.4\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 3.70 (t, 8H, $J=4.6\text{Hz}$, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{COO}-$).

IR

$\nu(\text{CO})=1,727\text{ cm}^{-1}$, $\nu(\text{allyl C}=\text{C})=1,647\text{ cm}^{-1}$

s=3

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 ^1H -NMR

δ (ppm) 6.92 (d, 3H, $J=13.9\text{Hz}$, $-\text{OCOCH}=\text{CHCOO}-$), 6.87 (d, 3H, $J=13.9\text{Hz}$, $-\text{OCOCH}=\text{CHCOO}-$), 5.96-5.86 (m, 3H, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 5.30 (d, 3H, $J=17.1\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 5.22 (d, 3H, $J=10.3\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 4.38 (t, 6H, $J=4.6\text{Hz}$, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{COO}-$), 4.31 (s, 6H, $\text{C}-\text{CH}_2-$), 4.04 (d, 6H, $J=5.9\text{Hz}$, $\text{CH}_2=\text{CH}-\text{CH}_2-$), 3.70 (t, 6H, $J=4.6\text{Hz}$, $-\text{O}-\text{CH}_2-\text{CH}_2-\text{COO}-$), 3.63 (s, 2H, $\text{C}-\text{CH}_2-$).

IR

$\nu(\text{CO})=1,727\text{ cm}^{-1}$, $\nu(\text{allyl C}=\text{C})=1,647\text{ cm}^{-1}$

(Example 6)

Into a 3 L-volume glass flask, 500.2 g of mono-2-allyloxyethyl fumarate obtained in Example 2 and 1.8 kg of THF were charged. The inside of the reaction system was purged with nitrogen and then, 345.1 g of potassium carbonate was added. After the completion of heat generation, the mixture was stirred for 1 hour and the reaction solution was cooled with ice water. Separately, a THF solution was prepared by dissolving 524.3 g of p-toluenesulfonyl chloride in 200 g of THF. When the temperature of the reaction solution reached 10°C or less, the p-toluenesulfonyl chloride/THF solution prepared was added and the reaction solution was stirred for 30 minutes. Thereafter, 93.2 g of trimethylolpropane and 691.0 g of potassium carbonate were added and stirred. After the completion of heat generation, the ice water was removed and the reaction solution was returned to a room temperature and further stirred for 2 hours.

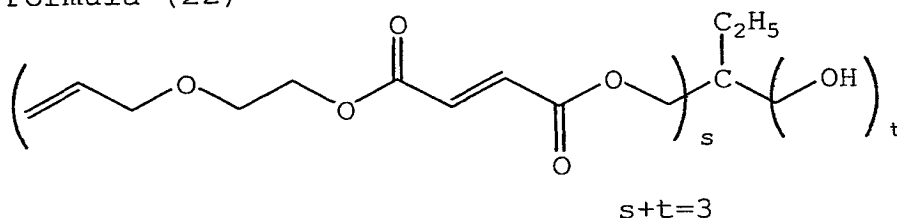
Then, the reaction solution was concentrated, the concentrate was transferred to a separatory funnel, 2 kg of ethyl acetate was added, and the separation washing was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was concentrated under reduced pressure to obtain 267 g of a product. $^1\text{H-NMR}$, FT-IR and GPC of the product were measured and this product was identified as a condensate of

trimethylolpropane with mono-2-allyloxyethyl fumarate, represented by formula (22).

IR

$$\nu(\text{CO})=1,727 \text{ cm}^{-1}, \nu(\text{allyl C}=\text{C})=1,647 \text{ cm}^{-1}$$

5 Formula (22)



The area percentage in the chart of analysis results by GPC of the product obtained is shown in Table 3 with respect to the value of s in formula (22).

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Table 3

Value of s	3	$2 \geq$
Compositional ratio (area % by GPC)	91.8	8.2

(Example 7)

Into a 1 L-volume round bottom flask equipped with a magnetic stirrer, a Dimroth condenser and a nitrogen inducing tube, 118.19 g of cyclohexanediol monoallyl ether, 148.71 g of maleic anhydride, 268 mg of hydroquinone monomethyl ether and 363 g of toluene were charged, and the mixture was stirred under heating at 110°C for 24 hours in a nitrogen atmosphere. To the reactant obtained, 12.6 g of concentrated hydrochloric acid and 267 mg of hydroquinone

monomethyl ether were added. The resulting mixture was heated under reflux for 5 hours in a nitrogen atmosphere and then cooled. The white precipitate deposited was separated by filtration through a 0.1 μm membrane filter and the filtrate was separated with water (500 ml \times 3 times). The obtained organic layer was dried over anhydrous magnesium sulfate and concentrated under reduced pressure by an evaporator, as a result, 162.49 g of a pale yellow viscous liquid was obtained. $^1\text{H-NMR}$ and FT-IR of the product were measured and this product was identified as a mono-2-allyloxycyclohexyl fumarate.

IR

$\nu(\text{COOH})=3,300\text{ cm}^{-1}$ – $2,500\text{ cm}^{-1}$, $\nu(\text{CO})=1,723\text{ cm}^{-1}$,

$\nu(\text{allyl C=C})=1,646\text{ cm}^{-1}$

15

(Example 8)

Into a 1 L-volume glass flask equipped with a stirring unit, a thermometer, a condenser and distilling receiver with stopcock, 161.53 g of mono-2-allyloxycyclohexyl fumarate obtained in Example 7, 103.37 g of cyclohexanediol monoallyl ether, 262.37 g of toluene, 8.6 g of p-toluenesulfonic acid and 520 mg of tetrakis[methylene-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate]methane ("IRGANOX 1010", trade name, produced by Chiba Specialty Chemicals) as a polymerization inhibitor were charged.

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The mixture was refluxed under heating in an oil bath, and the reaction was continued while distilling off the water generated as a by-product with the progress of the reaction. When the amount of water distilled off reached the

5 theoretical amount, the reaction was finished and the reaction solution was cooled. This reaction solution was transferred to a separatory funnel, 300 ml of toluene was added thereto, and the separation was performed using an aqueous 1N sodium hydroxide solution and water. Thereafter,

10 the resulting solution was dried over sodium sulfate and concentrated under reduced pressure to obtain 230.28 g of a product. Thus obtained crude product was purified with a column chromatography as shown below.

130 g of silica gel (WAKO-GEL C-200, trade name,

15 produced by Wako Jyunyaku Kogyo K.K.) in hexane slurry was filled in a chromato-column of 5 cm in diameter.

20.2 g of the crude product obtained above was charged in the chromato-column and eluted using ethyl acetate/hexane=1/10 as a developer to collect a fraction

20 having an R_f value of 0.52 of the thin layer chromatography ("Pre-coated TLC Plates SILICA GEL 60 F-254", produced by MERCK). Thereafter, this fraction was concentrated under reduced pressure by an evaporator, as a result, 15.1 g of a pale yellow oily liquid was obtained. ¹H-NMR, FT-IR and GPC

of the product were measured and this product was identified as a bis(2-allyloxycyclohexyl) fumarate.

IR

$\nu(\text{CO})=1,721 \text{ cm}^{-1}$, $\nu(\text{allyl C}=\text{C})=1,647 \text{ cm}^{-1}$

5

(Example 9)

Into a 500 ml-volume glass flask equipped with a stirring unit, a thermometer, a condenser and distilling receiver with stopcock, 53.9 g of mono-2-allyloxycyclohexyl fumarate obtained in Example 7, 6.0 g of pentaerythritol, 50 ml of toluene, 811.8 mg of p-toluenesulfonic acid and 54.6 mg of hydroquinone monomethyl ether were charged. The mixture was refluxed under heating in an oil bath, and the reaction was continued while distilling off the water generated as a by-product with the progress of the reaction. When the amount of water distilled off reached the theoretical amount, the reaction was finished and the reaction solution was cooled. This reaction solution was transferred to a separatory funnel, 300 ml of ethyl acetate was added thereto, and the separation was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the resulting solution was dried over sodium sulfate and concentrated under reduced pressure to obtain 38.9 g of a product.

^1H -NMR, FT-IR, GC and GPC of the product were measured and this product was identified as a composition containing a condensate of pentaerythritol with mono-2-allyloxycyclohexyl fumarate, and 40% (by GC) of bis(2-allyloxycyclohexyl) fumarate monomer.

IR

$\nu(\text{CO})=1,723\text{ cm}^{-1}$, $\nu(\text{allyl C=C})=1,645\text{ cm}^{-1}$

(Example 10)

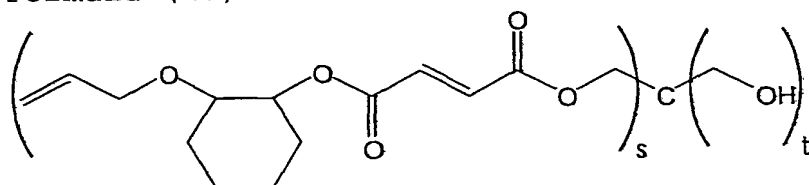
10 Into a 3 L-volume glass flask equipped with a stirring unit, 60.8 g of mono-2-allyloxycyclohexyl fumarate obtained in Example 7 and 200 ml of THF were charged. The inside of the reaction system was purged with nitrogen and then 22 g of potassium carbonate was added. After the completion of
15 heat generation, the mixture was stirred for 1 hour and the reaction solution was cooled with ice water. When the temperature of the reaction solution reached 10°C or less, 7.6 g of p-toluenesulfonyl chloride was added and stirred for 30 minutes. Thereafter, 5.4 g of pentaerythritol was
20 added and stirred. The reaction solution was returned to a room temperature and stirred for 12 hours. Then, the reaction solution was concentrated, the concentrate was transferred to a separatory funnel, 500 ml of ethyl acetate was added, and the separation washing was performed using
25 an aqueous 10% sodium carbonate solution and water.

Thereafter, the resulting solution was concentrated under reduced pressure to obtain 30 g of a product. $^1\text{H-NMR}$, FT-IR and GPC of the product were measured and the product was identified as a condensate of pentaerythritol with mono-2-allyloxycyclohexyl fumarate, represented by formula (23).

IR

$$\nu(\text{CO})=1,723 \text{ cm}^{-1}, \nu(\text{allyl C=C})=1,645 \text{ cm}^{-1}$$

Formula (23)



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$$s+t=4$$

The area percentage in the chart of analysis results by GPC of the product obtained is shown in Table 4 with respect to the value of s in formula (23).

15 Table 4

Value of s	4	3	$2 \geq$
Compositional ratio (area % by GPC)	82.2	2.0	15.8

(Example 11)

Into a 3 L-volume glass flask equipped with a dropping funnel, 1,400 g of allyl alcohol and 351.6 g of alumina (Alumina N Super I, trade name, produced by ICN) were

20

charged. Also 500g of styrene oxide was added through the dropping funnel while stirring under heating at 50°C in a nitrogen atmosphere. After the completion of the addition, heating and stirring were continued for 10 hours. After
5 cooling, the alumina was separated by filtration through a 0.1 µm membrane filter and the excess allyl alcohol was evaporated under reduced pressure from the reaction solution by an evaporator. Thereafter, the concentrated solution was distilled under reduced pressure to obtain 592
10 g (yield: 80%) of a mixture of 2-allyloxy-1-phenyl ethanol and 2-allyloxy-2-phenyl ethanol.

IR

$\nu(\text{OH})=3,443 \text{ cm}^{-1}$, $\nu(\text{Ph, CH})=3,050 \text{ cm}^{-1}$ - $3,030 \text{ cm}^{-1}$,

$\nu(\text{allyl C=C})=1,647 \text{ cm}^{-1}$

15 b.p. = 136°C (13 Torr)

(Example 12)

Into a 2 L-volume round bottom flask equipped with a induced magnetic stirrer, a Dimroth condenser and a
20 nitrogen inducing tube, 322.9 g of 2-allyloxyphenyl ethanol obtained in Example 11, 354.9 g of maleic anhydride, 1.36 g of hydroquinone monomethyl ether and 677.5 g of toluene were charged, and the mixture was stirred under heating at 130°C in an oil bath for 5 hours in a nitrogen atmosphere.
25 After cooling, 80 g of concentrated hydrochloric acid was

added to the reactant obtained. The resulting mixture was stirred under heating at 130°C in an oil bath for 10 hours in a nitrogen atmosphere and then cooled. The precipitated fumaric acid was separated by filtration and the filtrate was separated with water. The obtained organic layer was dried over anhydrous sodium sulfate and toluene was evaporated under reduced pressure by an evaporator. Thereafter, the reaction solution was introduced into hexane to precipitate a white solid. Then the white solid was separated by filtration and dried under reduced pressure to obtain 375.8 g (yield: 75.1%) of mono(2-allyloxy-phenylethyl) fumarate. The thus obtained white solid was used in the next process without further purification.

15 IR

$\nu(\text{COOH})=3,400\text{ cm}^{-1}$ - $2,560\text{ cm}^{-1}$, $\nu(\text{CO})=1,723\text{ cm}^{-1}$,

$\nu(\text{allyl C=C})=1,645\text{ cm}^{-1}$

m.p. = 71.2-71.4°C

20 (Example 13)

Into a 500 ml-volume glass flask equipped with a stirring unit, a thermometer, a condenser and distilling receiver with stopcock, 138.14 g of mono(2-allyloxy-phenylethyl) fumarate obtained in Example 12, 89.125 g of 2-allyloxyphenyl ethanol, 150 ml of benzene, 2.76 g of p-

toluenesulfonic acid and 138 mg of hydroquinone monomethyl ether as a polymerization inhibitor were charged. The mixture was refluxed under heating in an oil bath, and the reaction was continued while distilling off the water generated as a by-product with the progress of the reaction. When the amount of water distilled off reached the theoretical amount, the reaction was finished and the reaction solution was cooled. This reaction solution was transferred to a separatory funnel, 300 ml of benzene was added thereto, and the separation was performed using an aqueous 1% sodium hydroxide solution and water. Thereafter, the resulting solution was dried over sodium sulfate and concentrated under reduced pressure to obtain 200 g of a crude product. Thus obtained crude product was purified by re-crystallization in hot hexane to obtain a white solid. $^1\text{H-NMR}$, FT-IR and GPC of the thus obtained white solid were measured and this solid was identified as a bis(2-allyloxyphenylethyl) fumarate.

IR

$\nu(\text{Ph, CH})=3,050\text{ cm}^{-1}-3,030\text{ cm}^{-1}$, $\nu(\text{CO})=1,725\text{ cm}^{-1}$,
 $\nu(\text{allyl C=C})=1,647\text{ cm}^{-1}$

m.p. = 68.3-68.5°C

(Example 14)

Into a 1 L-volume glass flask, 75.7 g of mono(2-allyloxy-phenylethyl) fumarate obtained in Example 12 and 355.6 g of THF were charged. The inside of the reaction system was purged with nitrogen and then, 38 g of potassium carbonate was added. After the completion of heat generation, the mixture was stirred for 1 hour and the reaction solution was cooled with ice water. Separately, a THF solution was prepared by dissolving 51.5 g of p-toluenesulfonyl chloride in 89 g of THF. When the temperature of the reaction solution reached 10°C or less, the p-toluenesulfonyl chloride/THF solution prepared was added and the reaction solution was stirred for 30 minutes. Thereafter, 7.5 g of pentaerythritol and 82.2 g of potassium carbonate were added and stirred. After the completion of heat generation, the ice water was removed and the reaction solution was returned to a room temperature and further stirred for 5 hours.

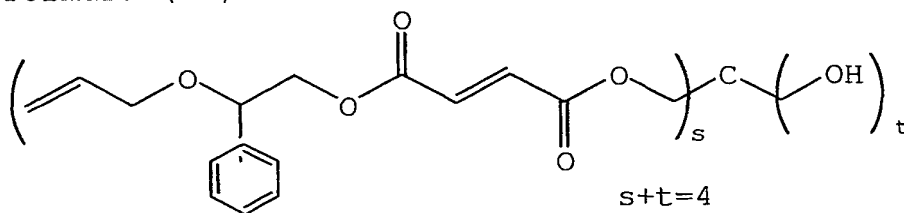
Then, the reaction solution was concentrated, the concentrate was transferred to a separatory funnel, 1 kg of ethyl acetate was added, and the separation washing was performed using an aqueous 10% sodium carbonate solution and water. Thereafter, the organic layer was concentrated under reduced pressure to obtain 32.5 g of a crude product. The thus obtained crude product was purified with a column chromatography as shown below.

1 kg of silica gel (WAKO-GEL C-200, trade name, produced by Wako Jyunyaku Kogyo K.K.) in hexane slurry was filled in a chromato-column of 10 cm in diameter. The crude product obtained above was charged in the chromato-column and eluted using ethyl acetate/hexane as a developer. By changing a ratio of the developer gradually from 1/20 to 1/5 to collect a fraction having an R_f value of 0.50 (developer: ethyl acetate/hexane=1/2) of the thin layer chromatography ("Pre-coated TLC Plates SILICA GEL 60 F-254", produced by MERCK). Thereafter, this fraction was concentrated under reduced pressure by an evaporator, as a result, 10.1 g of a pale yellow oily liquid was obtained. ¹H-NMR, FT-IR and GPC of the product were measured and this product was identified as a condensate of pentaerythritol with mono(2-allyloxy-phenylethyl) fumarate, represented by formula (24) and value of s is 4.

IR

 $\nu(\text{Ph, CH}) = 3,080 \text{ cm}^{-1} - 3,030 \text{ cm}^{-1}, \nu(\text{CO}) = 1,725 \text{ cm}^{-1},$
 $\nu(\text{allyl C=C}) = 1,647 \text{ cm}^{-1}$

20 Formula (24)



(Example 45)

Into a 300ml-volume glass flask equipped with a condenser, 20.0 g of fumaric acid, 37.22 g of cyclohexene oxide, 60.8 g of 1,4-dioxane and 3.7 g of alumina (Alumina N-Super I, trade name, produced by ICN Pharmaceuticals) were charged. After purging the reaction system with nitrogen, heating and stirring were continued at 60°C for 13.5 hours. Filtrating the resultant reaction solution through membrane filter and distilling off the filtrate under reduced pressure gave 40.7 g of transparent oily liquid.

Successively, into a 100 ml-volume glass flask equipped with a stirring unit, a thermometer, a condenser and distilling receiver with stopcock, 10.3 g of transparent oily liquid obtained above, 17 g of mono-2-allyloxycyclohexyl fumarate obtained in Example 7, 26.7 g of toluene, 338.2 mg of p-toluenesulfonic acid and 10 mg of hydroquinone monomethyl ether as a polymerization inhibitor were charged. The mixture was heated under reflux in an oil bath, and the reaction was continued while distilling off water generated as a by-product with the progress of the reaction. When the amount of water distilled off reached the theoretical amount, the reaction was finished and the reaction solution was cooled. Toluene was distilled off under reduced pressure from the reaction solution to obtain a viscous yellow liquid. And after a small amount of ethyl

acetate was added thereto, it was re-precipitated by introducing in hexane. Thus obtained white viscous solid was washed with water and further with hexane to obtain 15 g of white solid. $^1\text{H-NMR}$, FT-IR and GPC of the thus
5 obtained white solid were measured and this solid was identified as a polycondensate of 1,2-cyclohexanediol with fumaric acid and allyl alcohol.

IR

$$\nu(\text{CO})=1,722 \text{ cm}^{-1}, \nu(\text{allyl C=C})=1,647 \text{ cm}^{-1}$$

10

(Examples 15~20)

50 g of the mixture obtained in Example 3, 50 g of toluene, 10 mg of hydroquinone monomethyl ether (MEHQ) and 15 g of 5% Pd- Al_2O_3 were added and after purging the inside
15 of the reaction system with nitrogen, the mixture was stirred under heating at 140°C for 3 hours. After cooling, 5% Pd- Al_2O_3 was removed by filtration from the reaction solution and then toluene was distilled off under reduced pressure from the filtrate to obtain 48 g of a pale yellow
20 viscous liquid. $^1\text{H-NMR}$ was measured and by comparing the peaks of ally group and propenyl group, it was confirmed that 98% was isomerized into propenyl group.

The isomerization reaction of the mixtures obtained in Examples 4, 5, 6, 7 and 8 was performed by the same
25 operation. The results are shown together in Table 5.

Table 5

	Charging					Reaction Results
Example	Example where Starting Material used for Reaction is described	Starting Material (g)	Toluene (g)	Catalyst (g)	MEHQ (mg)	Isomerization ratio (%)
15	3	50	50	15	10	98
16	4	50	50	15	10	100
17	5	85	85	25	18	100
18	6	50	50	15	10	98
19	7	50	50	15	10	98
20	8	50	50	15	10	99

(Example 21)

34 g of the crude product obtained in Example 14, 90 g of toluene, 10 mg of hydroquinone monomethyl ether (MEHQ) and 3.13 g of carbonylchlorohydridetris(triphenylphosphine) ruthenium(II) were added and after purging the inside of the reaction system with nitrogen, the mixture was stirred under heating at 140°C for 3 hours. After cooling, toluene was distilled off under reduced pressure from the reaction solution to obtain 33 g of a pale yellow viscous liquid.

¹H-NMR was measured and by comparing the peaks of ally group and propenyl group, it was confirmed that 98% was isomerized into propenyl group.

15

(Examples 22 to 35)

The fumarate derivatives of the present invention obtained in the Examples above each was coated on a glass substrate and cured by UV or heat. The surface hardness of the cured film was examined. The surface hardness was
 5 determined in accordance with the pencil scratch test of JIS K 5400.

The results are shown in Table 6.

Table 6

Example	Fumarate Derivative	Curing Method	Curing Conditions		Pencil Hardness
			Initiator	Temperature-Time/UV Exposure	
22	Compound of Example 1	heat	none	150°C-1 h	5H
23	Compound of Example 3	heat	none	150°C-1 h	6H
24	Compound of Example 4	heat	DCP ¹⁾ 2%	150°C-0.5 h	6H
25	Compound of Example 5	heat	DCP ¹⁾ 2%	150°C-0.5 h	7H
26	Compound of Example 6	UV	IRG184 ²⁾ 5%	900 mj/cm ²	6H
27	Compound of Example 8	heat	none	150°C-1 h	7H
28	Compound of Example 9	UV	IRG184 ²⁾ 5%	300 mj/cm ²	7H
29	Compound of Example 10	UV	IRG184 ²⁾ 5%	300 mj/cm ²	6H
30	Compound of Example 14	heat	none	150°C-1 h	6H
31	Compound of Example 17	UV	IRG184 ²⁾ 5%	300 mj/cm ²	7H

32	Compound of Example 17	heat	none	150°C-1 h	8H
33	Compound of Example 18	heat	none	150°C-1 h	7H
34	Compound of Example 20	UV	IRG184 ²⁾ 5%	300 mj/cm ²	7H
35	Compound of Example 21	heat	none	150°C-1 h	6H
Comparative Example 1	Compound of Comparative Example 1	UV	IRG184 ²⁾ 5%	1200 mj/cm ²	HB
Comparative Example 2	Compound of Comparative Example 2	heat	DCP ¹⁾ 2%	150°C-1 h	2H

1) DCP : Dicumyl Peroxide

2) IRG184: IRGACURE184, 1-Hydroxy-Cyclohexyl-phenyl-keton, trade name, produced by Chiba Specialty Chemicals

5 (Comparative Example 1)

Into a 1 L-volume flask equipped with a distillation unit, 144 g of dimethyl fumarate, 245 g of ethylene glycol monoallyl ether, 0.2 g of dibutyltin oxide were charged. The mixture was heated at 140°C in a nitrogen atmosphere and methanol generated as a by-product was distilled off. When methanol reached 70% of the theoretical amount, the pressure inside of the reaction system was gradually reduced to accelerate the distillation of methanol, and by finally reducing the pressure to about 400 Pa, the theoretical amount of methanol and the residual ethylene

glycol monoallyl ether were completely distilled off. The reaction solution was cooled to a room temperature and then 283 g of a product was taken out. ^1H -NMR and FT-IR of the product obtained were measured and this product was
5 identified as bis(2-allyloxyethyl) fumarate.

This product was coated on a glass substrate and cured by UV. The surface hardness of the cured film was examined. The surface hardness was determined in accordance with the pencil scratch test of JIS K 5400.

10 The results are shown in Table 6 above.

(Comparative Example 2)

Into a 1 L-volume flask equipped with a distillation unit, 144 g of dimethyl fumarate, 279 g of hydroxybutyl
15 vinyl ether, 0.2 g of zinc acetate and 0.3 g of IRGANOX 1010 as a polymerization inhibitor were charged. The mixture was heated to 140°C in a nitrogen atmosphere and methanol generated as a by-product was distilled off. When methanol reached 70% of the theoretical amount, the
20 pressure inside of the reaction system was gradually reduced to accelerate the distillation of methanol, and by finally reducing the pressure to about 400 Pa, the theoretical amount of methanol and the residual hydroxybutyl vinyl ether were completely distilled off. The

reaction solution was cooled to a room temperature and then 297 g of bis(4-vinyloxybutyl) fumarate was obtained.

This product was coated on a glass substrate and cured by heat. The surface hardness of the cured film was
5 examined. The surface hardness was determined in accordance with the pencil scratch test of JIS K 5400.

The results are shown in Table 6 above.

(Examples 36 to 42, 46 and Comparable Examples 3 to 4)

10 A composition of the fumarate derivative of the present invention was coated on a PET film or a glass substrate and cured by UV or heat. The surface hardness of the cured film was examined. The tack-free coating having
no tackiness on the cured surface was rated ○ and the
15 coating having tackiness was rated ×.

The curing was performed under the following conditions.

(i) Heat curing

Temperature 150°C-1 hour

20 (ii) UV curing

Initiator: IRGACURE-184, 5%

Exposure: 300 mj/cm²

The results are shown in Table 7 blow.

Table 7

	Example 36	Example 37	Example 38	Example 39	Example 40	Example 41	Example 42	Example 46	Comparative Example 3	Comparative Example 4
Blend- ing, % by weight	Compound of Example 1	50	50	80	50	80	60	70	100	100
	Compound of Example 10									
	Compound of Example 15									
	Compound of Example 17									
	Compound of Example 18									
	PE-TA ³⁾									
	80MFA ⁴⁾	30	50	20	50	20	20	30	100	100
	8524 ⁵⁾									
	BPF ⁶⁾									
	Curing Method	(i)	(i)	(i)	(ii)	(ii)	(ii)	(i)	(i)	(ii)
Film Pro- per- ties	Tack	O	O	O	O	O	O	O	X	O
	Pencil hardness	5H	6H	7H	6H	2H	2H	5H	-	F
Substrate		glass	glass	glass	glass	PET	PET	glass	glass	PET

3) PE-TA: pentaerythritol triacrylate,

4) Epoxy Ester 80MFA: epoxy acrylate, trade name, produced by Kyo-ei-Sha Kagaku.

5) Unsaturated Polyester 8524: trade name, produced by Japan U-PICA Co. Ltd.

6) BPF: bis[2-(1-propenyloxy)ethyl fumarate]

(Example 43)

After bis(2-allyloxy-phenylethyl) fumarate as described in Example 13 was melted at 80°C, 2% by mass of 1,1-bis(tert-hexylperoxy)3,3,5-trimethyl cyclohexane as a radical polymerization initiator was added thereto and the polymerizable composition was cured by casting at a temperature of 110°C (1 hour), successively at 130°C (1 hour). The refractive index of the obtained cured product was measured, and n_D was 1.5573.

10

(Example 44)

1% by mass of tert-hexylperoxy 2-ethylhexanoate as a radical polymerization initiator was added to the condensate of pentaerythritol with mono(2-allyloxy-phenylethyl) fumarate as described in Example 14, and the polymerizable composition was cured by casting at a temperature of 80°C (1 hour), successively at 120°C (1 hour). The refractive index of the obtained cured product was measured, and n_D was 1.5520.

20

(Comparative Example 5)

2% by mass of 1,1-bis(tert-hexylperoxy)3,3,5-trimethyl cyclohexane as a radical polymerization initiator was added to bis(2-allyloxyethyl) fumarate as described in Comparative Example 1, and casting cured

25

the polymerizable composition. The refractive index of the obtained cured product was measured, and n_D was 1.5132.

5

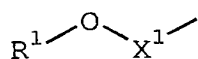
Effects of the Invention

As described in the foregoing pages, the fumarate derivative of the present invention has the terminal alkenyloxy group which copolymerizability is high as compared with conventional fumarate derivatives, so that the crosslinking degree can increase and a cured product having excellent surface hardness can be provided. Also, the composition thereof with other polymerizable compounds can be used similarly for the purpose of improving the curability and the surface hardness. Moreover, a cured product made of the fumarate derivative containing an aryl group of the present invention has high refractive index of equal to or more than 1.55. Therefore, the cured product of the present invention is expected to apply for use of high refractive index.

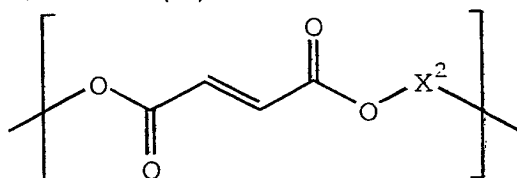
CLAIMS

1. A fumarate derivative having at least one group represented by formula (1) as the terminal groups and having two or more groups represented by formula (2) as a repeating unit:

Formula (1)

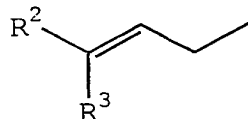


Formula (2)



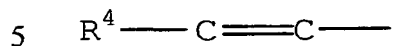
- 10 (wherein in formula (1), each R^1 independently represents formula (3) or (4), and in formula (1) or (2), X^1 and X^2 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and 2 to 30 carbon atoms, provided
- 15 that X^1 and X^2 may be ester-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) as a repeating unit);

Formula (3)



(wherein R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms);

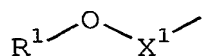
Formula (4)



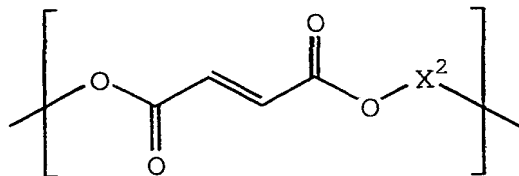
(wherein R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).

2. A fumarate derivative having at least one group
10 represented by formula (1) as the terminal groups and having two or more groups represented by formula (2) and/or formula (5) as a repeating unit:

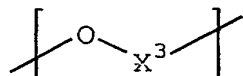
Formula (1)



15 Formula (2)



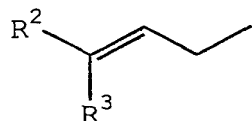
Formula (5)



(wherein in formula (1), each R^1 independently
20 represents formula (3) or (4), and in formulae (1), (2) and (5), X^1 , X^2 and X^3 each independently represents an organic residue derived from a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to

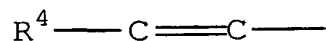
30 carbon atoms, provided that X^1 , X^2 and X^3 may be ester-bonded and/or ether-bonded to have a branched structure having a group represented by formula (1) as the terminal groups and having a group represented by formula (2) and/or formula (5) as a repeating unit);

Formula (3)



(wherein R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms);

Formula (4)



(wherein R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).

15

3. The fumarate derivative as claimed in claim 1 or 2, wherein the number of repetitions of the repeating unit represented by formula (2) is any one in the range from 2 to 10.

20

4. The fumarate derivative as claimed in claim 2 or 3, wherein the number of repetitions of the repeating unit represented by formula (5) is any one in the range from 2 to 5.

5. The fumarate derivative as claimed in any one of claims 1 to 4, wherein 80% or more of R^1 in formula (1) is formula (4).

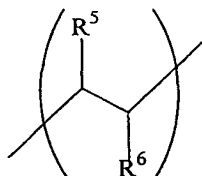
5

6. The fumarate derivative as claimed in any one of claims 1 to 5, wherein R^4 in formula (4) is any one selected from the group consisting of hydrogen atom, a methyl group, an ethyl group, an n-propyl group and an
10 isopropyl group.

7. The fumarate derivative as claimed in any one of claims 1 to 6, wherein X^1 , X^2 and X^3 in formulae (1), (2) and (5) each independently is an organic residue
15 derived from at least one alcohol selected from the group consisting of an alkylene diol, an alicyclic diol and an aromatic diol.

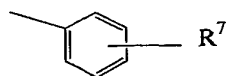
8. The fumarate derivative as claimed in any one of
20 claims 1 to 7, wherein the organic residue as claimed in claim 7 is represented by formula (6).

Formula (6)



(wherein R^5 and R^6 each independently represents hydrogen atom or formula (7));

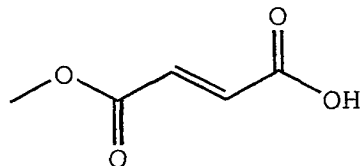
Formula (7)



5 (wherein R^7 represents hydrogen atom or an alkyl group having from 1 to 3 carbon atoms).

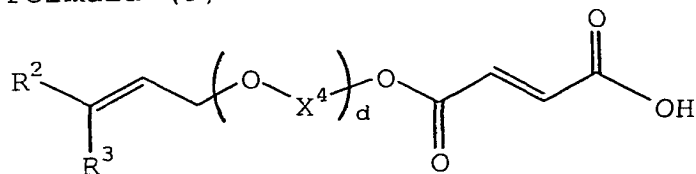
9. The fumarate derivative as claimed in any one of claims 1 to 8, wherein at least one terminal group is a
10 group represented by formula (8):

Formula (8)



10. The fumarate derivative, which is represented by
15 formula (9):

Formula (9)

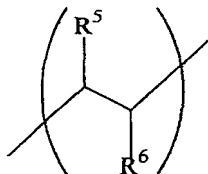


(wherein each X^4 , which is present in the number of d in formula (9), independently represents an alkylene group or a cycloalkylene group having from 5 to 12
20 carbon atoms, d represents an integer of 1 to 5, and R^2

and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms).

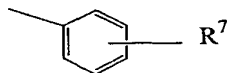
11. The fumarate derivative as claimed in claim 10,
5 wherein X^4 in formula (9) is an alkylene group represented in formula (6).

Formula (6)



- (wherein R^5 and R^6 each independently represents
10 hydrogen atom or formula(7));

Formula (7)



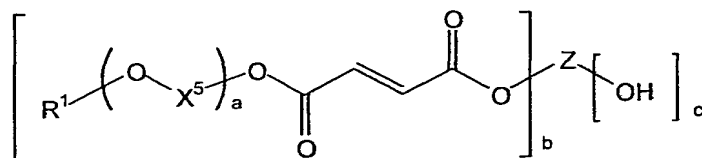
- (wherein R^7 represents hydrogen atom or an alkyl
group having from 1 to 3 carbon atoms).

15

12. The fumarate derivative as claimed in any one of
claims 1 to 9, wherein at least one terminal group is a
hydroxyl group.

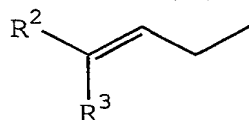
- 20 13. The fumarate derivative, which is represented by
formula (10):

Formula (10)



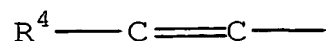
(wherein Z represents an organic residue derived from a tri-, tetra-, penta- or hexa-hydric alcohol, R^1 independently represents formula (3) or formula (4),
 5 each X^5 , which is present in the number of a in formula (10), independently represents an alkylene group or a cycloalkylene group having from 5 to 12 carbon atoms, a represents an integer of 1 to 5, b represents an integer of 1 to 6, c represents an integer of 0 to 5,
 10 and $b+c$ is from 3 to 6);

Formula (3)



(wherein R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5
 15 carbon atoms);

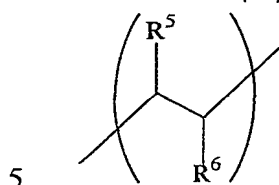
Formula (4)



(wherein R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).

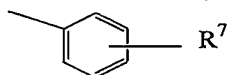
14. The fumarate derivative as claimed in claim 13, wherein X^5 in formula (10) is an alkylene group represented in formula (6).

Formula (6)



(wherein R^5 and R^6 each independently represents hydrogen atom or formula (7));

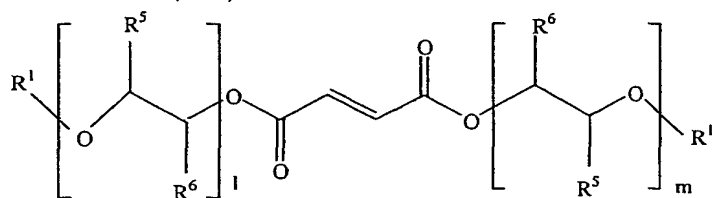
Formula (7)



10 (wherein R^7 represents hydrogen atom or an alkyl group having from 1 to 3 carbon atoms).

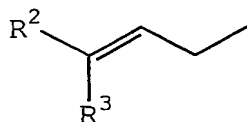
15. The fumarate derivative, which is represented by formula (11):

15 Formula (11)



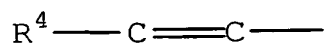
(wherein, R^1 independently represents formula (3) or formula (4), and l and m each independently represents an integer of 1 to 5);

20 Formula (3)



(wherein R^2 and R^3 each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms);

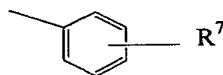
5 Formula (4)



(wherein R^4 represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).

(wherein R^5 and R^6 each independently represents
10 hydrogen atom or formula(7));

Formula (7)



(wherein R^7 represents hydrogen atom or an alkyl group having from 1 to 3 carbon atoms).

15

16. A method for producing a fumarate derivative as claimed in any one of claims 1 to 9 and claim 12, comprising reacting a fumarate derivative having at least one formula (8) in the terminal groups and having
20 two or more groups represented by formula (2) as a repeating unit with a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms in the presence of a catalyst.

17. A method for producing a fumarate derivative as claimed in claim 13 or 14, comprising reacting a fumarate derivative having at least one group
- 5 represented by formula (8) in the terminal groups with a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms in the presence of a catalyst.
- 10 18. A method for producing a fumarate derivative as claimed in any one of claims 1 to 9 and claim 12, comprising reacting a fumarate derivative having at least one group represented by formula (8) in the terminal groups and having two or more groups
- 15 represented by formula (2) as a repeating unit with a polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms in the presence of a condensing agent and a base.
- 20 19. A method for producing a fumarate derivative as claimed in claim 13 or 14, comprising reacting a fumarate derivative having at least one group represented by formula (8) in the terminal groups with a polyhydric alcohol having from 2 to 6 hydroxyl groups

and having from 2 to 30 carbon atoms in the presence of a condensing agent and a base.

20. A method for producing a fumarate derivative as
5 claimed in claims 18 and 19, wherein the condensing agent is sulfonyl chloride.

21. The method for producing a fumarate derivative as
claimed in any one of claims 16 to 20, wherein the
10 polyhydric alcohol having from 2 to 6 hydroxyl groups and having from 2 to 30 carbon atoms is at least one selected from the group consisting of trimethylolpropane, trimethylolethane, pentaerythritol, ditrimethylolpropane, dipentaerythritol and adducts
15 thereof with an ethylene oxide or a propylene oxide.

22. A method for producing a fumarate derivative having formula (4) in the terminal groups, comprising isomerizing terminal groups of a fumarate derivative
20 having formula (3) as the terminal groups in the presence of a catalyst to convert said terminal groups into formula (4).

23. The method for producing a fumarate derivative
25 having formula (4) in the terminal groups as claimed in

claim 22, wherein the fumarate derivative having formula (3) as the terminal groups is the fumarate derivative described in any one of claims 1 to 15.

5 24. The method for producing a fumarate derivative having formula (4) in the terminal groups as claimed in claim 22 or 23, wherein 80% or more of the fumarate derivative having formula (3) as the terminal groups is converted into formula (4) by the isomerization
10 reaction.

25. The method for producing a fumarate derivative having formula (4) in the terminal groups as claimed in claim 22 or 23, wherein the catalyst used for the
15 isomerization reaction is a catalyst containing at least one of palladium, rhodium and ruthenium.

26. A polymerizable composition comprising the fumarate derivative as claimed in any one of claims 1
20 to 15.

27. The polymerizable composition as claimed in claim 26, which comprises:

from 1 to 99% by mass of the fumarate derivative
25 described in any one of claims 1 to 15, and

from 1 to 99% by mass of at least one compound selected from the group consisting of an unsaturated polyester, an oligomer having (meth)acrylate group and a radical polymerizable monomer.

5

28. A polymerizable composition comprising:

100 parts by mass of the polymerizable composition described in claim 26 or 27, and

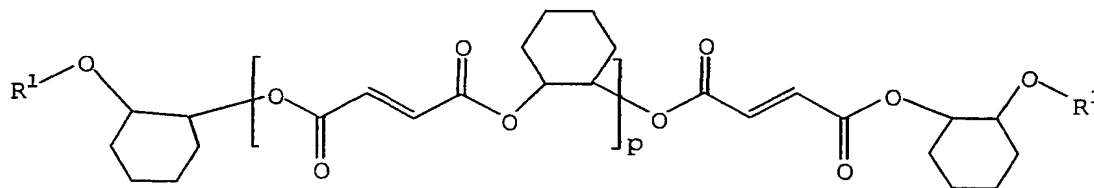
from 0.01 to 15 parts by mass of a radical
10 polymerization initiator.

29. A cured product obtained by curing the polymerizable composition as claimed in any one of claims 26 to 28.

15

30. The fumarate derivative, which is represented by formula (25):

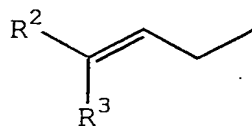
Formula (25)



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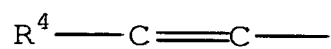
(wherein, R¹ independently represents formula (3) or formula (4), and p represents an integer of 1 to 9);

Formula (3)



(wherein R² and R³ each independently represents hydrogen atom or an alkyl group having from 1 to 5 carbon atoms);

5 Formula (4)



(wherein R⁴ represents hydrogen atom or an alkyl group having from 1 to 11 carbon atoms).